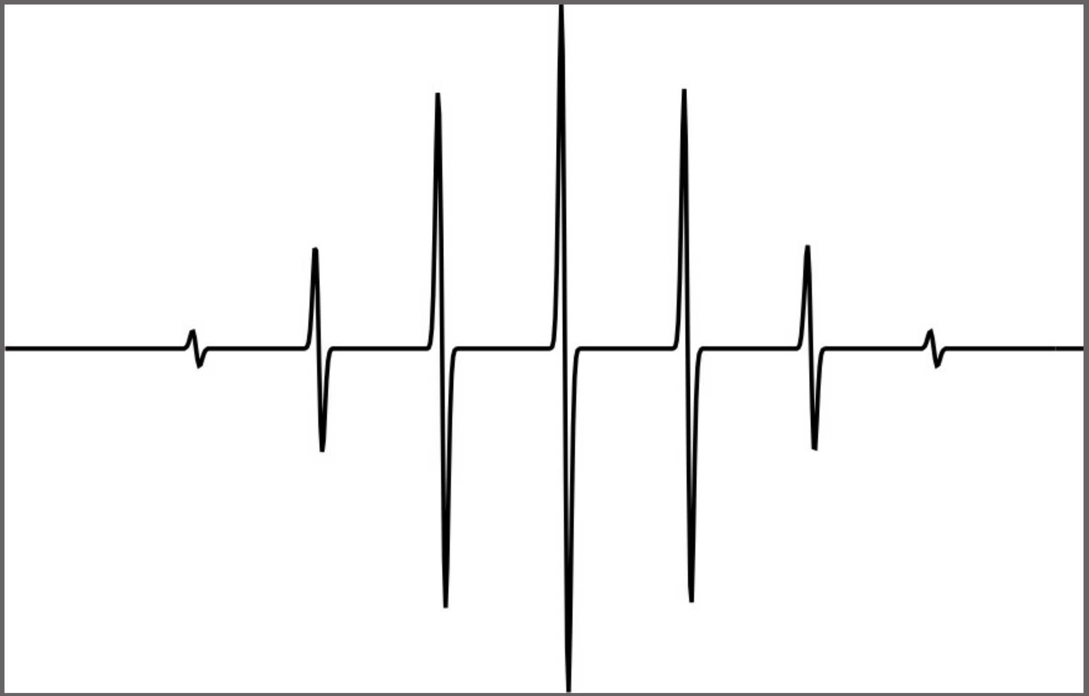
ELECTRON SPIN RESONANCE SPECTROCOPY



Contents

Electron Spin Resonance Spectroscopy

- It is a branch of absorption spectroscopy in which radiation having frequency in microwave region is absorbed by paramagnetic substance to induce transition between magnetic energy level of electron with unpaired spins.
- Magnetic energy splitting is done by applying a static magnetic field.
- Absorption spectroscopy, operate at microwave frequency $10^4 – 10^6$ MHz (~1.0 J mol-1)

- ESR Phenomenon is shown by:

1. Atoms having odd number of electrons.
2. Ions having partly filled inner electron shells
3. Other molecules that carry angular momentum of electronic origin.
4. Free radicals having unpaired electrons.
5. Molecules with paired electrons and zero magnetic field.

- ESR is also known as Electron Paramagnetic Resonance(EPR) or Electron Magnetic Resonance(EMR).
- Paramagnetic substances are those which contains unpaired electrons having equal and opposite spins.
- They are of two types:

1. Stable paramagnetic substances. Eg. NO, $O_{2,}$ $NO_{2.}$
2. Unstable paramagnetic Substances Eg. Free radicals.

Theory of ESR

- In ESR the energy levels are produced by the interaction of magnetic moment of an unpaired electron in a molecule or ion with an applied magnetic field.
- Required frequency of radiation dependent upon strength of magnetic field
  - Common field strength 0.34 and 1.24 T
  - 9.5 and 35 GHz
  - Microwave region
- The ESR spectrum results due to the transitions between these energy levels by absorbing radiations of microwave frequency.

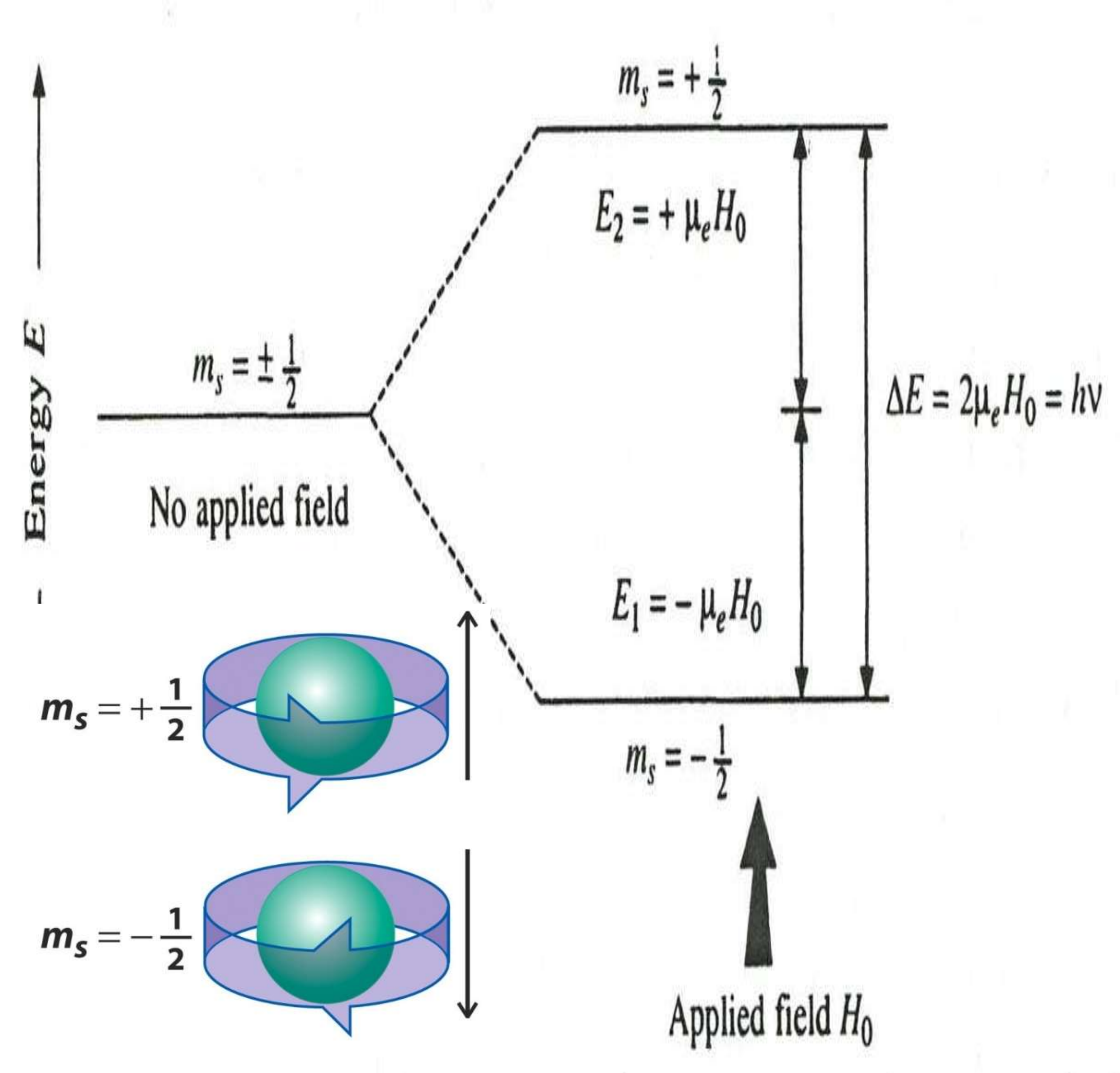
- The unpaired electrons are excited to a high energy state under the magnetic field by the absorption of microwave radiations.
- The excited electron changes its direction of spin and relaxes in to the ground state by emitting its energy.
- The transition between two different energy levels takes place by absorbing a quantum of radiation of frequency in the microwave region.Unlike most traditional spectroscopy techniques, in EPR spectroscopy the frequency of the radiation is held constant while the magnetic field is varied in order to obtain an absorption spectrum.

Energy Levels

- The unpaired electrons are excited to a high energy state under the magnetic field by the absorption of microwave radiations.

- The excited electron changes its direction of spin and relaxes in to the ground state by emitting its energy.

- The transition between two different energy levels takes place by absorbing a quantum of radiation of frequency in the microwave region.



- When absorption takes place:

$$2\mu_e H = h\nu$$

- Where v =frequency of absorbed radiation in cycles/second.
- The energy of transition is given by

$$\Delta E = hv = g\,\mu_B H$$

Where h = Plank's constant

H = Applied magnetic filed

μ_B = Bohr' s magneton which is a factor for converting angular momentum into magnetic moment.

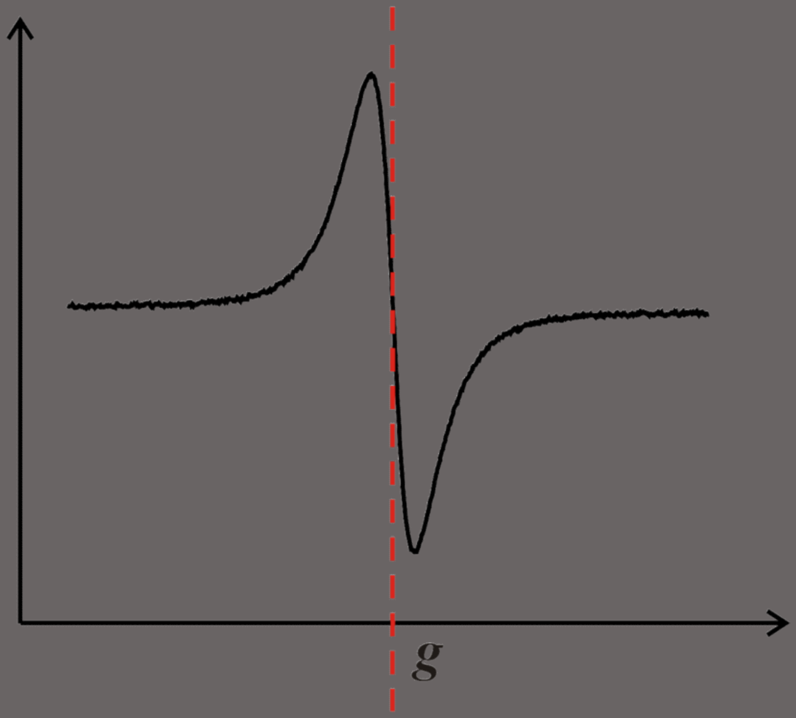
The value of μ_B is given as $\mu_B = eh/4\pi mc$

Where, e = electric charge

m = mass of electron

c = velocity of light

Proportionality Factor



- Measured from the center of the signal
- For a free electron
  - 2.00232
- For organic radicals
  - Typically close to free-electron value
  - 1.99-2.01
- For transition metal compounds
  - Large variations due to spin-orbit coupling and zero-field splitting
  - 1.4-3.0

Instrumentation

- Source
- Circulator or Magic -T
- Sample Cavity
- Magnet System
- Crystal Detector
- Auto amplifier and Phase sensitive Detector
- Oscilloscope and Pen Recorder

Source:

- Klystron

- It is a vacuum tube which can produce microwave oscillations centered on a small range of frequency

- The frequency of the monochromatic radiation is determined by the voltage applied to Klystron.

Isolator:

- It is a non reciprocal device which minimizes vibrations in the frequency of microwaves produced by Klystron oscillator.
- The variations occur in the frequency due to the backward reflections in the region between the Klystron and circulator.
- Isolator is a strip of ferrite material.

Wave meter

- It is fixed in between the isolator and attenuator to know the frequency of microwaves produced by Klystron oscillator.

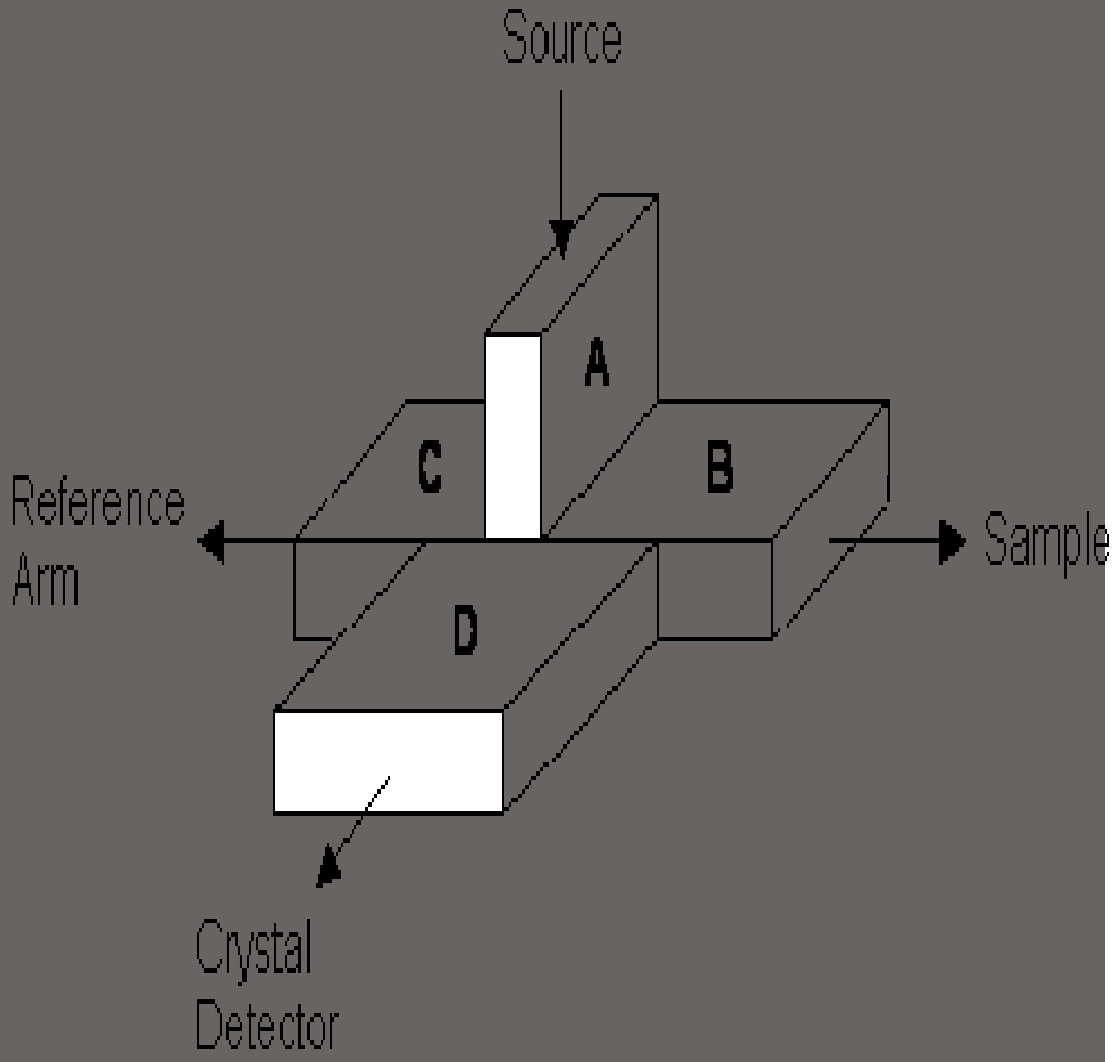
- Usually it is calibrated in frequency units instead of wavelength.

Attenuator:

- Attenuator is used to adjust the level of the microwave power incident upon the sample.
- It processes an absorption element and corresponds to a neutral filter in light absorption measurement.

Magic T or Circulator:

- Microwave radiations finally enter to the circulator through a wave guide by a loop wire which couples with oscillating magnetic field and setting a corresponding field.



Sample Cavity:

- This resonant cavity which contains the sample is called the heart of ESR.
- It is constructed in such a way to maximize the applied magnetic filed along the sample dimension.
- In most ESR spectrometer dual sample cavities are used for simultaneous observation of sample and reference materials.

Magnet System:

- The sample cavity is placed between the pole pieces of an electromagnet
- This provides a homogenous magnetic field and can be varied from zero to 500 gauss.
- The stability of the field is achieved by energizing the magnet with a highly regulated power supply.

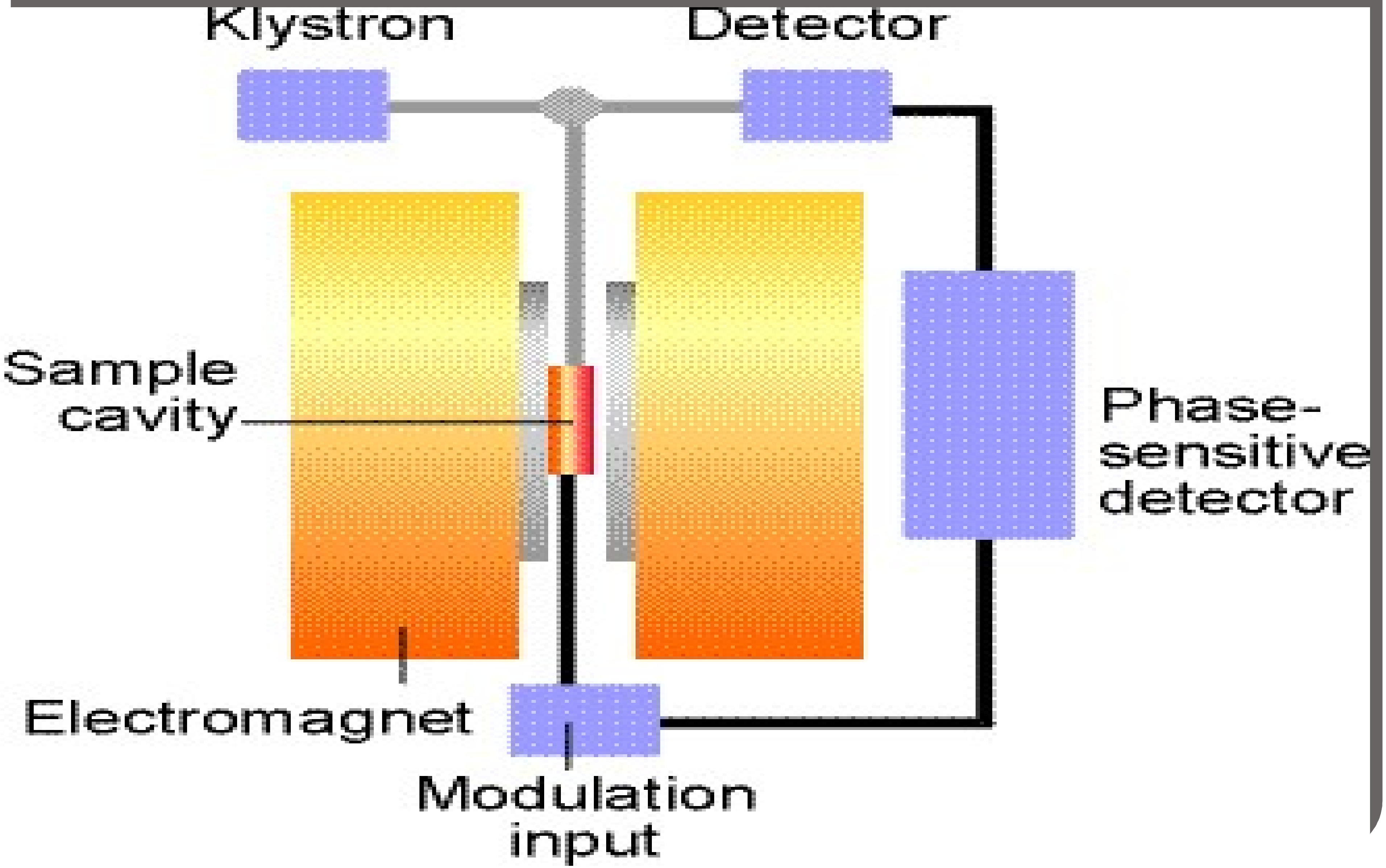
Crystal Detectors:

- The most commonly used detector is a silicon crystal which acts as a microwave rectifier.
- This converts microwave power into a direct current input.

Oscilloscope and Pen Recorder

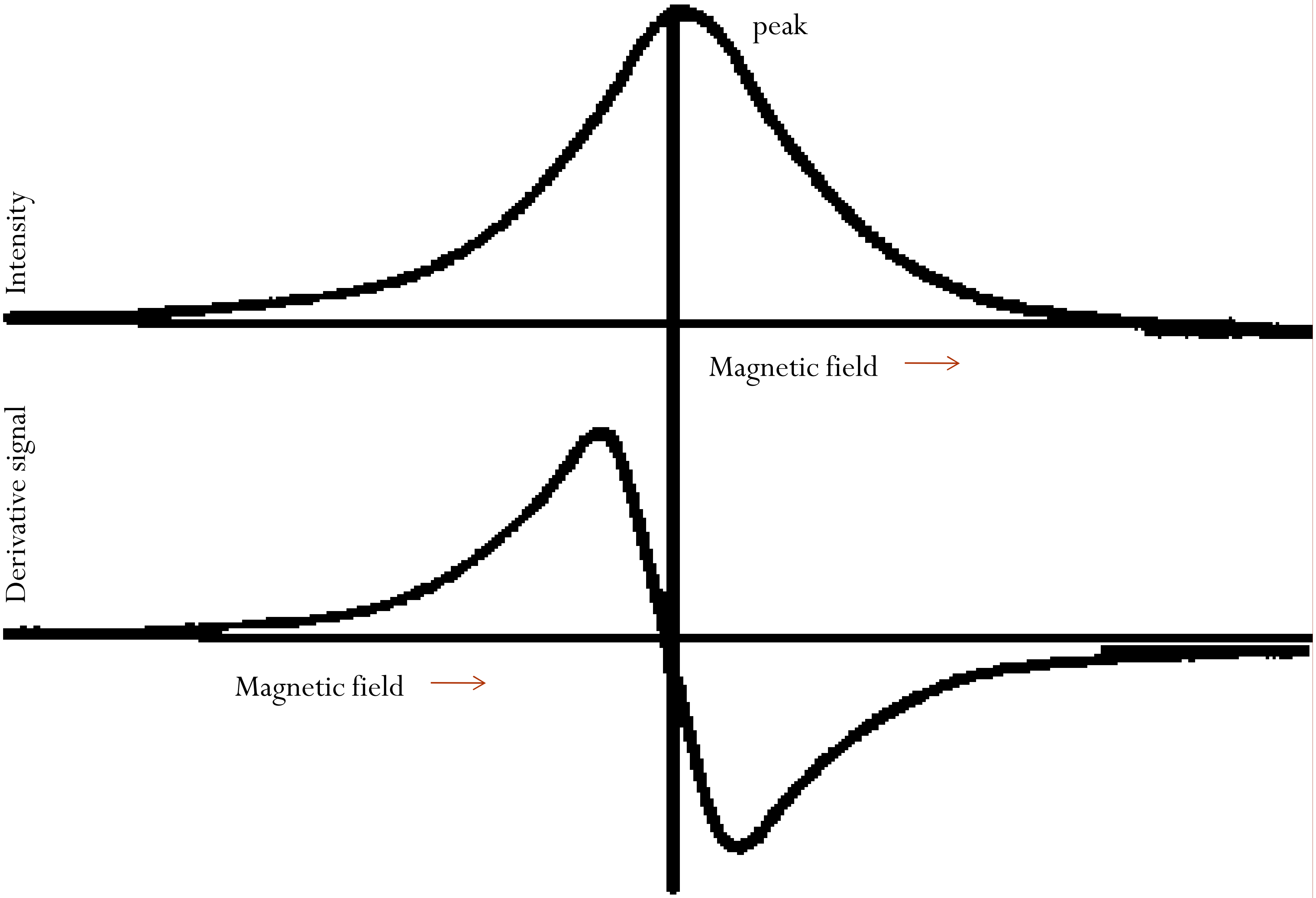
- The signal from phase sensitive detector and sweep unit is recorded by the oscilloscope or pen recorder.

ESR Spectrometer:



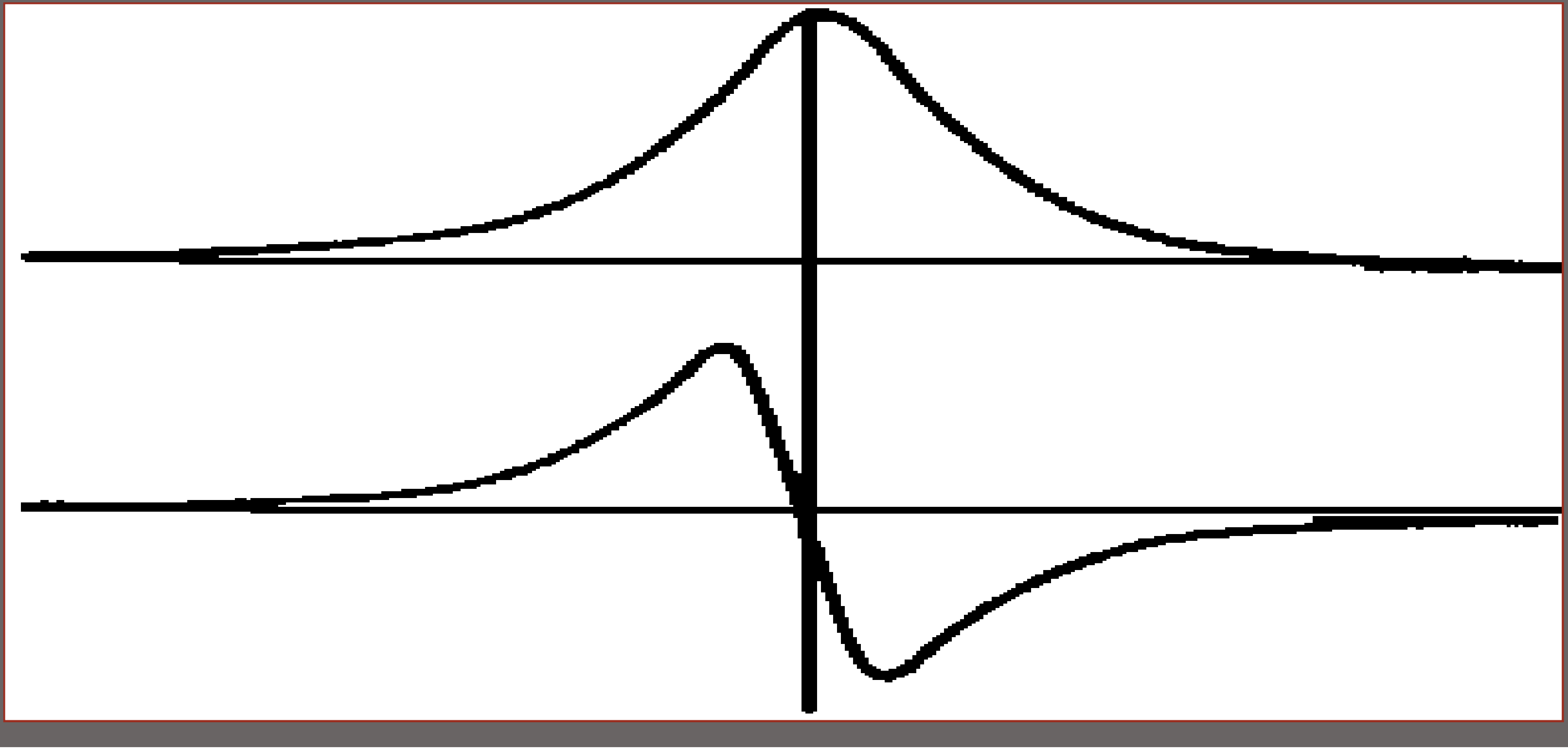
Working:

- The Klystron oscillator is set to produce microwaves.
- After passing though the isolator, wave meter and attenuator the microwaves are entered into the circulator on magic T
- Then it reaches the detector which acts as a rectifier, ie. converting the microwave power into the direct current.
- If the magnetic field around the resonating cavity having the sample is changed to the value required for the resonance, the recorder will show an absorption peak.
- If the magnetic field is swept slowly over a period of several minutes, the recorder will show the derivative of the microwave absorption spectrum against magnetic field as shown below:

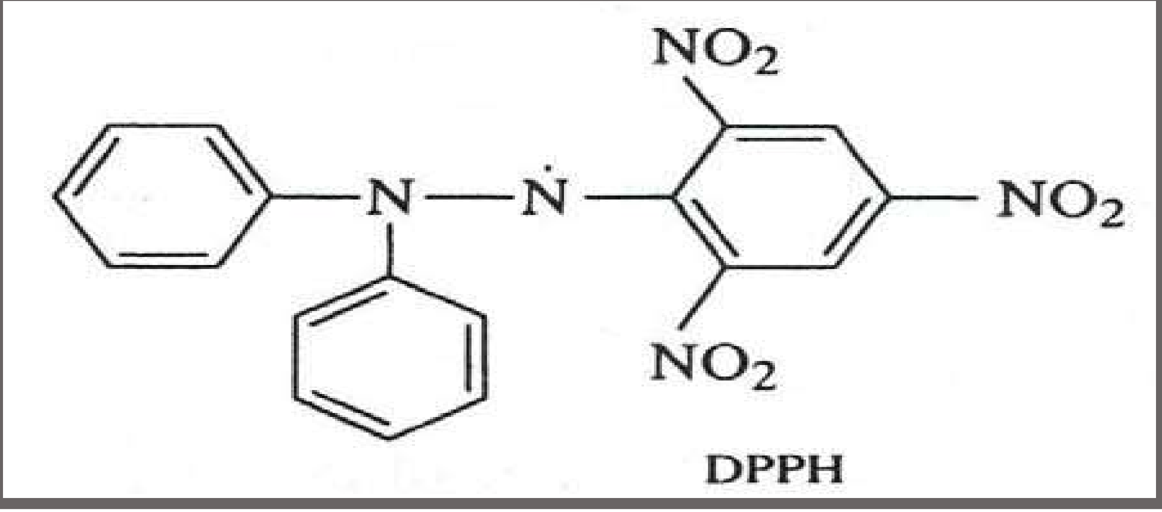

peak
Intensity
Magnetic field →
Derivative signal
Magnetic field →

Presentation of ESR Spectrum:

- The ESR spectrum is obtained by plotting intensity against the strength of a magnetic field.
- The better way is to represent ESR spectrum as a derivative curve in which the first derivative(slope) of the absorption curve is plotted against the strength of the magnetic field



- The total area covered by either the absorption or derivative curve is proportional to the number of unpaired electrons in the sample.
- In order to find out the number of electrons in an unknown sample, comparison is made with a standard sample having a known number of unpaired electrons and possessing the same line shape as the unknown.
- The most widely used standard is 1,1-diphenyl-2-picrylhydrazyl free radical(DPPH)



DPPH

Determination of g value:

- The best method of measurement of g value is to measure the field separation between the center of the unknown spectrum and that of reference substance whose g value is already known.
- DPPH is generally used a standard whose g value is 2.0036.
- In the spectrometer standard sample is placed along with the unknown sample in the same chamber of dual cavity cell.
- The spectrum will show signals with a filed separation of ΔH.
- The g value of unknown sample is given

$$\mathbf{g = g_s [\, \Delta H/H \,]}$$

Hyperfine Interactions

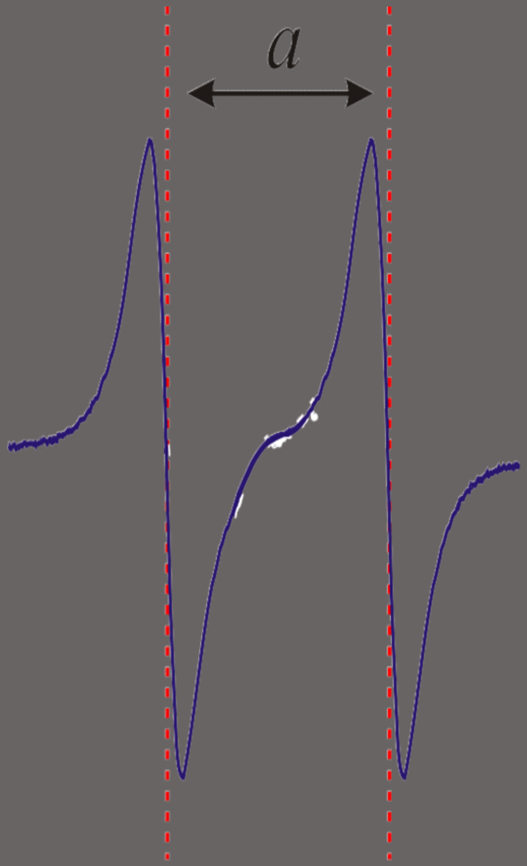
- EPR signal is ‘split’ by neighboring nuclei
  - Called hyperfine interactions
- Can be used to provide information
  - Number and identity of nuclei
  - Distance from unpaired electron
- Interactions with neighboring nuclei

$$E = g\mu_B B_0 M_S + aM_s m_I$$

a = hyperfine coupling constant

m_I = nuclear spin quantum number

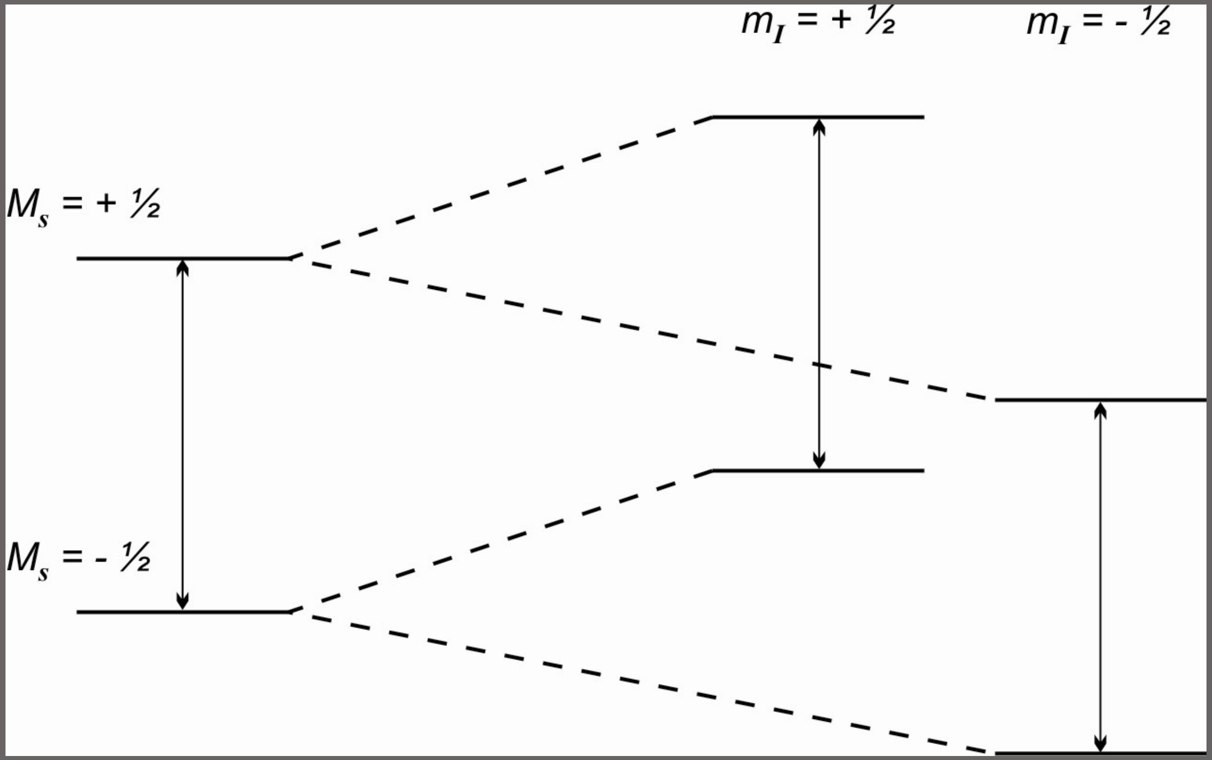
- A is measured as the distance between the centers of two signals



Which nuclei will interact?

- Selection rules same as for NMR
- Every isotope of every element has a ground state nuclear spin quantum number, ***I***
  - has value of $\boldsymbol{n}/2$, $\boldsymbol{n}$ is an integer
- Isotopes with even atomic number and even mass number have ***I*** $= 0$, and have no EPR spectra
  - ^{12}C, ^{28}Si, ^{56}Fe, …
- Isotopes with odd atomic number and even mass number have ***n*** even
  - ^{2}H, ^{10}B, ^{14}N, …
- Isotopes with odd mass number have ***n*** odd
  - ^{1}H, ^{13}C, ^{19}F, ^{55}Mn, …

Hyperfine Interactions



Interaction with a single nucleus of spin ½

Ebsworth, E. A. V.; Rankin, David W. H.; Cradock, Stephen *Structural Methods in Inorganic Chemistry*; CRC Press: Boca Raton, 1987.

Hyperfine Interactions

- Coupling patterns same as in NMR
- More common to see coupling to nuclei with spins greater than ½
- The number of lines:

$$2NI + 1$$

N = number of equivalent nuclei

I = spin

- Only determines the number of lines--not the intensities

Hyperfine Interactions

- Relative intensities determined by the number of interacting nuclei

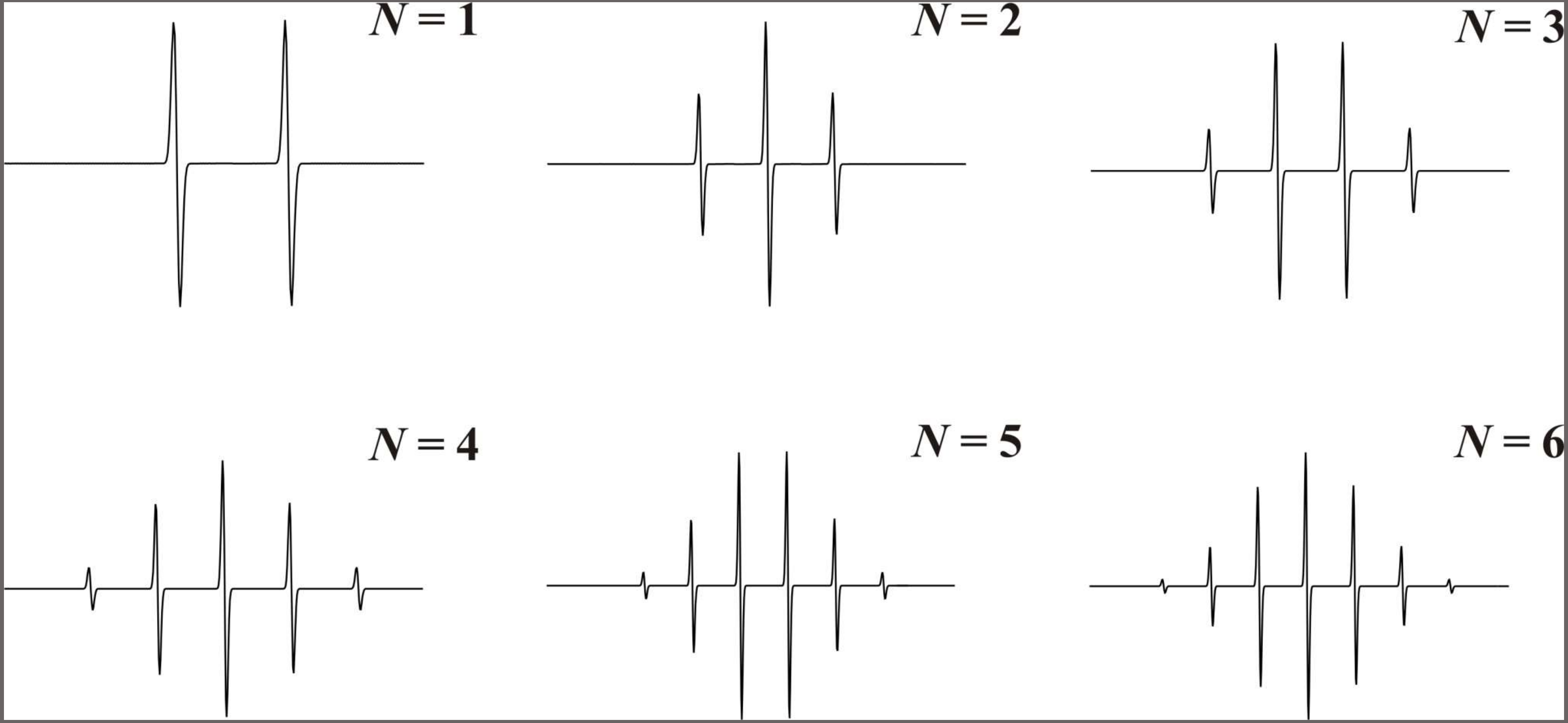
- If only one nucleus interacting
  - All lines have equal intensity

- If multiple nuclei interacting
  - Distributions derived based upon spin
  - For spin ½ (most common), intensities follow binomial distribution

Relative Intensities for $I = ½$

N	Relative Intensities
0	1
1	1 : 1
2	1 : 2 : 1
3	1 : 3 : 3 : 1
4	1 : 4 : 6 : 4 : 1
5	1 : 5 : 10 : 10 : 5 : 1
6	1 : 6 : 15 : 20 : 15 : 6 : 1

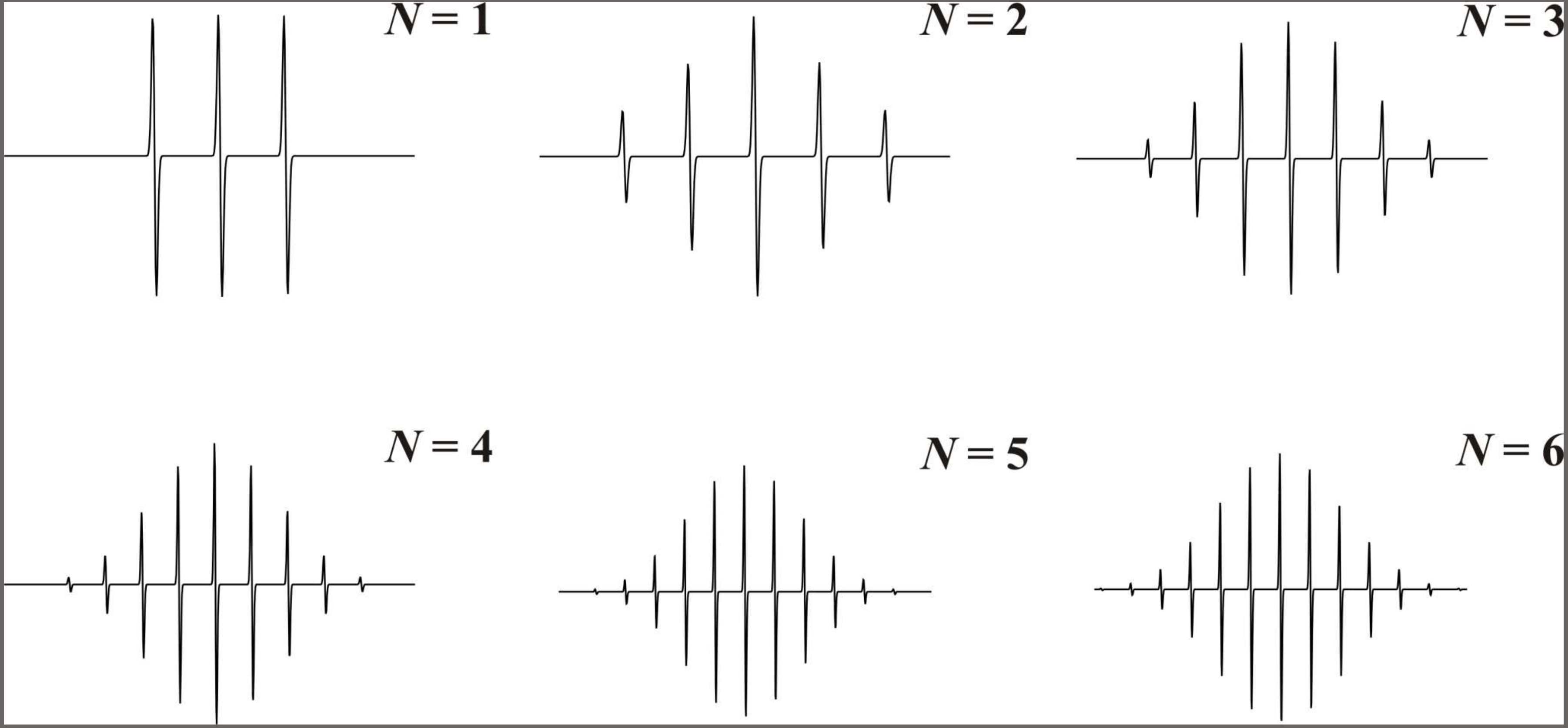
Relative Intensities for $I = \frac{1}{2}$



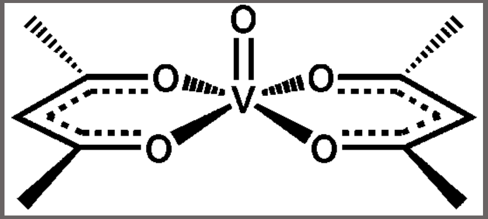
Relative Intensities for I = 1

N	Relative Intensities
0	1
1	1 : 1 : 1
2	1 : 2 : 3 : 2 : 1
3	1 : 3 : 6 : 7 : 6 : 3 : 1
4	1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1
5	1 : 5 : 15 : 20 : 45 : 51 : 45 : 20 : 15 : 5 : 1
6	1 : 6 : 21 : 40 : 80 : 116 : 141 : 116 : 80 : 40 : 21 : 6 : 1

Relative Intensities for $I = 1$



Hyperfine Interactions

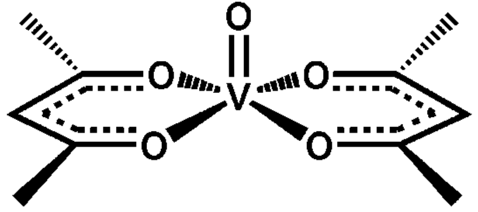


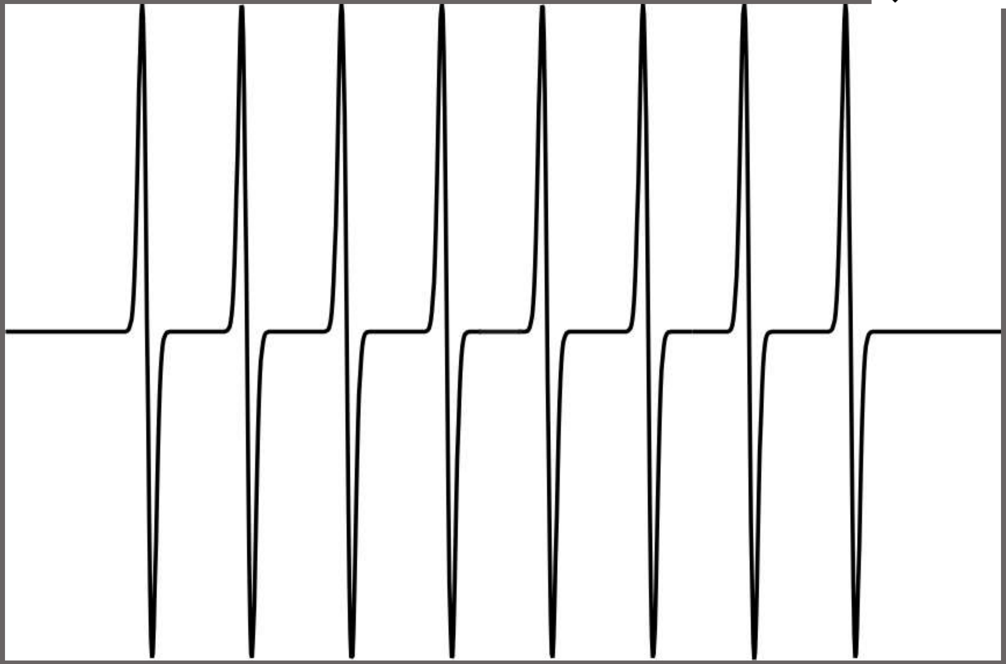
- Example:
  - VO(acac)$_2$
  - Interaction with vanadium nucleus
  - For vanadium, $\boldsymbol{I} = 7/2$
  - So,

$$2\boldsymbol{NI} + 1 = 2(1)(7/2) + 1 = 8$$

  - You would expect to see 8 lines of equal intensity

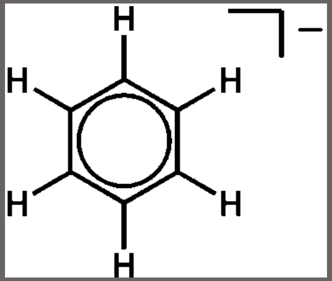
Hyperfine Interactions





EPR spectrum of vanadyl acetylacetonate

Hyperfine Interactions

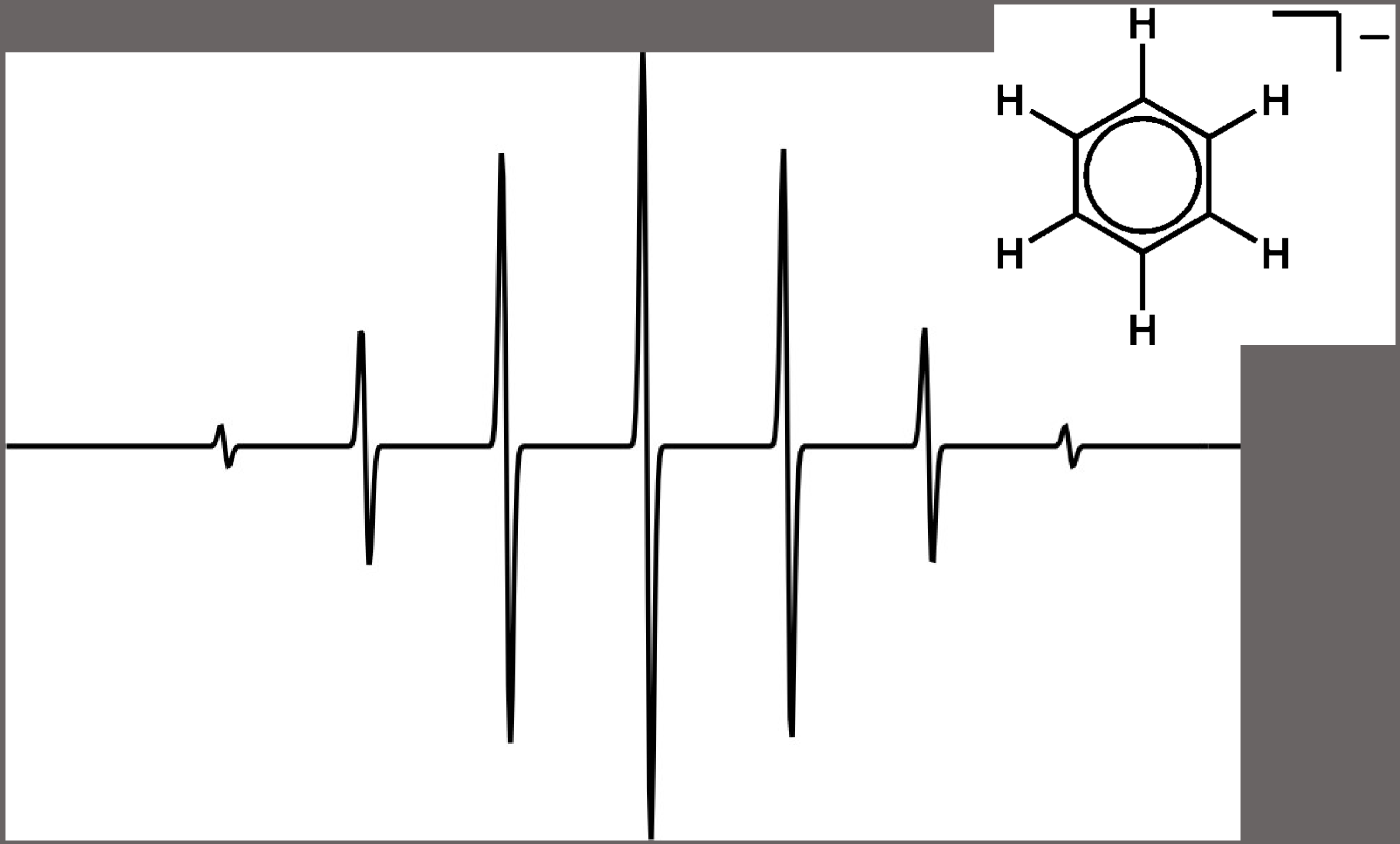


- Example:
  - Radical anion of benzene $[C_6H_6]^-$
  - Electron is delocalized over all six carbon atoms
    - Exhibits coupling to six equivalent hydrogen atoms
  - So,

$$2NI + 1 = 2(6)(1/2) + 1 = 7$$

  - So spectrum should be seven lines with relative intensities 1:6:15:20:15:6:1

Hyperfine Interactions

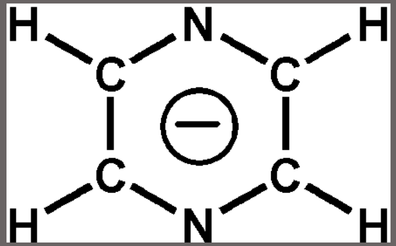


EPR spectrum of benzene radical anion

Hyperfine Interactions

- Coupling to several sets of nuclei
  - First couple to the nearest set of nuclei
    - Largest ***a*** value
  - Split each of those lines by the coupling to the next closest nuclei
    - Next largest ***a*** value
  - Continue 2-3 bonds away from location of unpaired electron

Hyperfine Interactions



- Example:
  - Pyrazine anion
  - Electron delocalized over ring
    - Exhibits coupling to two equivalent N ($I = 1$)

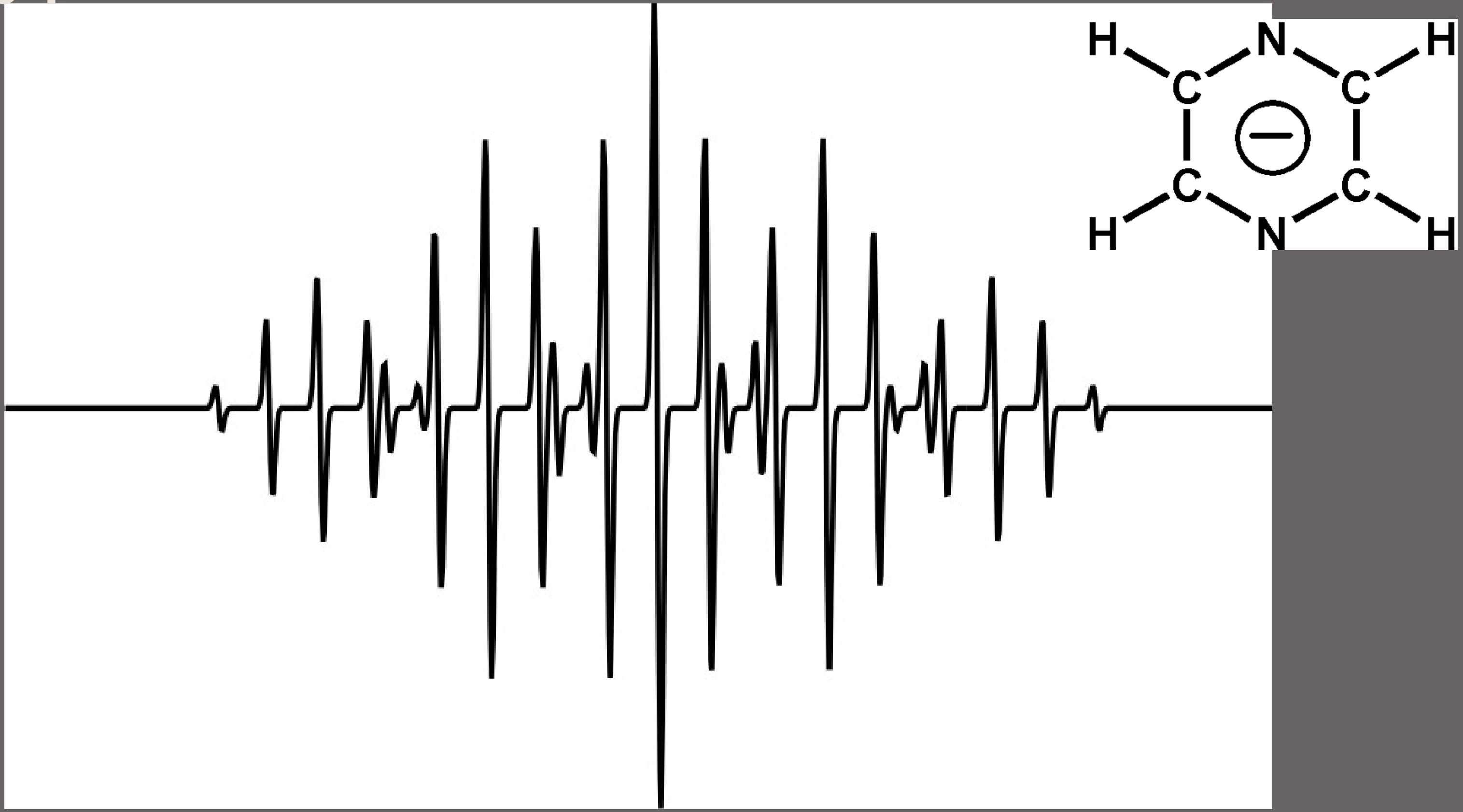
$$2NI + 1 = 2(2)(1) + 1 = 5$$

    - Then couples to four equivalent H ($I = ½$)

$$2NI + 1 = 2(4)(1/2) + 1 = 5$$

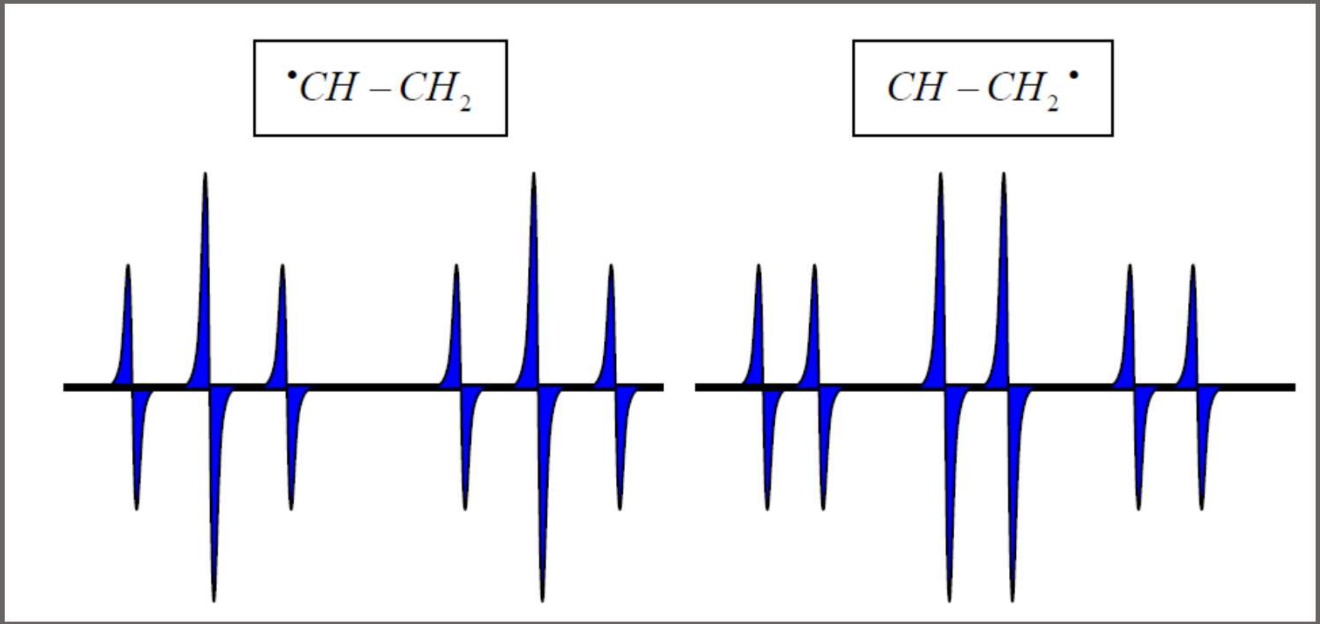
  - So spectrum should be a quintet with intensities 1:2:3:2:1 and each of those lines should be split into quintets with intensities 1:4:6:4:1

Hyperfine Interactions



EPR spectrum of pyrazine radical anion

- Let us predict the E.S.R spectrum of the radical fragment CH CH2 • − It should contain six lines - a large doublet arising from the interaction with the CH fragment (producing two lines) and a smaller triplet due to the electron interacting more weakly with the two remote protons of the CH2 fragment (producing three lines). The resulting diagram is shown in Figure. In the case where the radical is CH CH2 • − , the resulting pattern is also predicted to contain six lines, now triplet will have large compare to doublets as shown in Figure



Conclusions

- Analysis of paramagnetic compounds
  - Compliment to NMR
- Examination of proportionality factors
  - Indicate location of unpaired electron
    - On transition metal or adjacent ligand
- Examination of hyperfine interactions
  - Provides information on number and type of nuclei coupled to the electrons
  - Indicates the extent to which the unpaired electrons are delocalized

Comparison of ESR with NMR

NMR	ESR
Different energy states are produced due to the alignment of the nuclear magnetic moments relative to applied magnetic field and the transition between these energy states occurs on the application of an appropriate frequency in the radio frequency region.	Different energy states are produced due to the alignment of the electronic magnetic moments relative to applied magnetic filed and the transition between these energy states occurs on the application of an appropriate frequency in the microwave region.
NMR absorption positions are expressed in terms of chemical shifts.	ESR absorption positions are expressed in terms of “g” values.
Nuclear spin spin coupling causes the splitting of NMR signals.	Coupling of the electronic spin with nuclear spins(hyperfine coupling) causes the splitting of ESR signals.

Applications of ESR spectroscopy:

Electron Paramagnetic Resonance (EPR), sometimes referred to as Electron Spin Resonance (ESR), is a widely accepted spectroscopic technique in various research fields. This technique is used to study paramagnetic centers on various oxide surfaces, which are frequently encountered in heterogeneous catalysis. The observed paramagnetic centers include surface defects, inorganic or organic radicals, metal cations or supported metal complexes and clusters. Each of these paramagnetic species will produce a characteristic EPR signature. Diamagnetic oxide materials can also be studied using suitable paramagnetic probes, including nitroxides and transition metal ions.

Applications

A. *Applications of ESR spectra:*

- It decides the site of unpaired electrons.
- The number of line components decide about the number and type of nuclei present in the neighborhood of the odd electron.
- If the electric field is not spherical then the ESR spectrum is anisotropic,ie the rotation of the sample shifts the ESR spectrum.
- From this the g value can be measured by comparing the position of the line with that of standard substance.
- Determination of type of nuclei which are responsible for splitting pattern by comparing the relative intencities.

Applications of ESR spectroscopy:

☐ **Study of Free radicals**

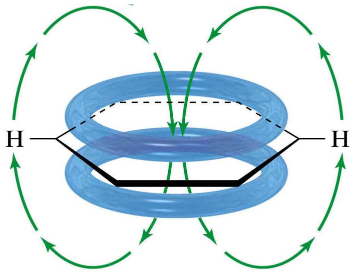
- Even in very low concentrations also we can study the free radicals by using ESR spectroscopy.
- Structure of organic and inorganic free radicals can be identified.
- Investigation of molecules in the triplet state.
- Spin label gives the information about polarity of its environment.

☐ **Structural Determination**

- In certain cases ESR provides the information about the shape of the radcals.

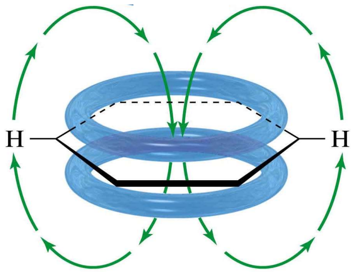
- ❑ **Reaction Velocities and Mechanisms**
- ❑ **Study of inorganic compounds**
- ❑ **Study of catalysts**
- ❑ **Determination of oxidation state of a metal.**
- ❑ ***Analytical applications:***
- Determination of Mn^{2+}
- Determination of vanadium.
- Determination of poly nuclear hydrocarbon.
- ❑ ***Biological applications:***
- The presence of free radicals in healthy and diseased conditions.
- Functioning of most of the oxidative enzymes can be conformed.

THANK YOU



Nuclear Magnetic Resonance Spectroscopy

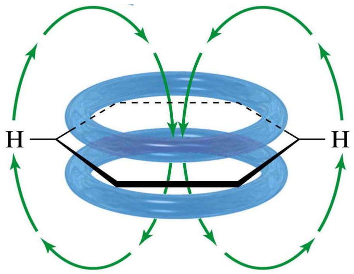
Introduction



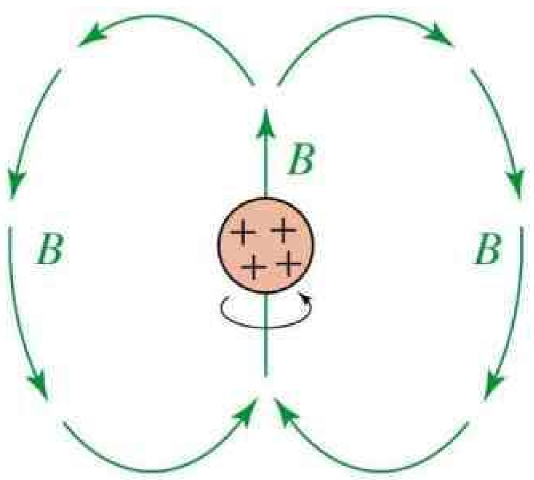
- NMR is the most powerful tool available for organic structure determination.
- It is used to study a wide variety of nuclei:
  - ^{1}H
  - ^{13}C
  - ^{15}N
  - ^{19}F
  - ^{31}P

=>

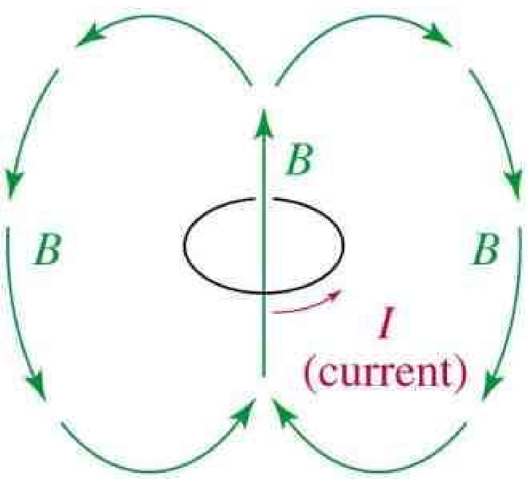
Nuclear Spin



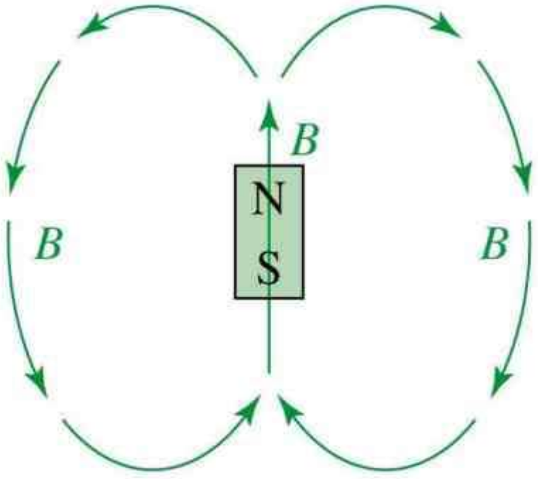
- A nucleus with an odd atomic number or an odd mass number has a nuclear spin.
- The spinning charged nucleus generates a magnetic field.



spinning proton

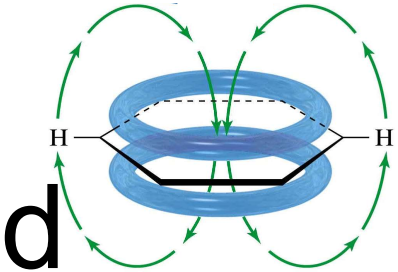


loop of current



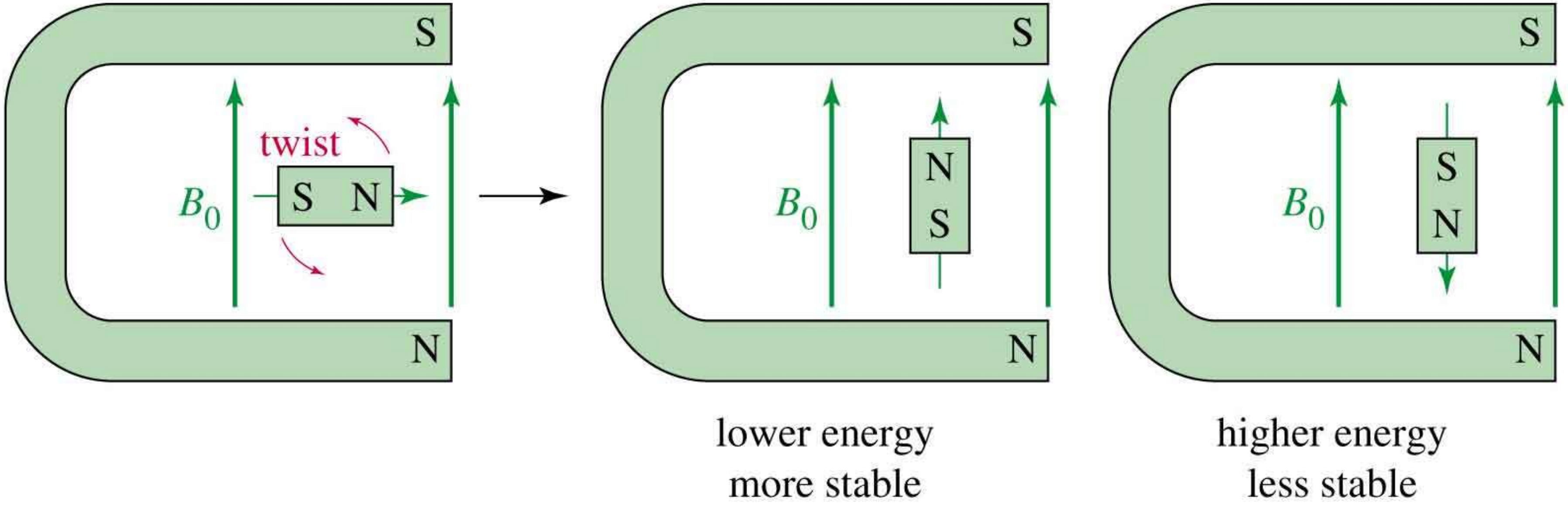
bar magnet

=>



External Magnetic Field

When placed in an external field, spinning protons act like bar magnets.



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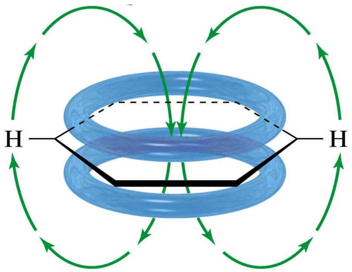
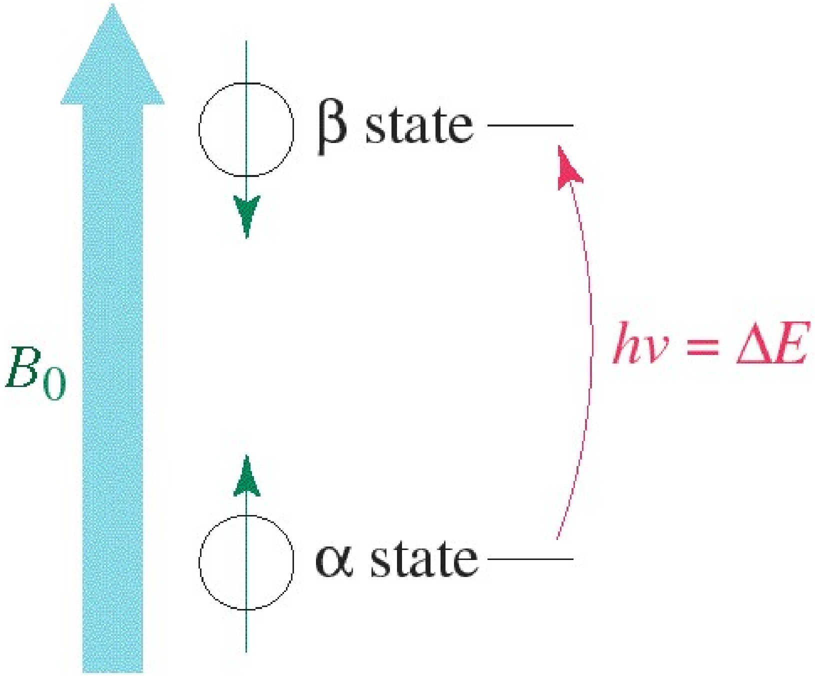
Two Energy States

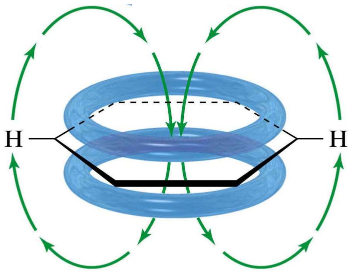


The magnetic fields of the spinning nuclei will align either *with* the external field, or *against* the field.

A photon with the right amount of energy can be absorbed and cause the spinning proton to flip. =>

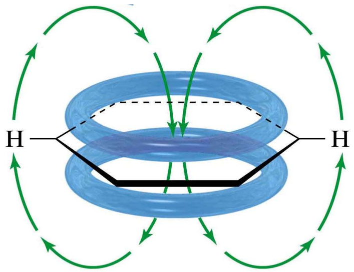


ΔE and Magnet Strength



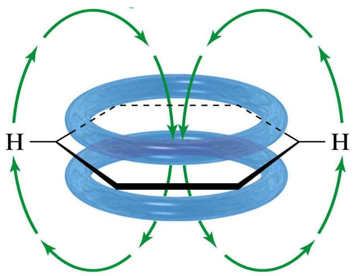
- Energy difference is proportional to the magnetic field strength.
- $\Delta E = h\nu = \gamma \frac{h}{2\pi} B_0$
- Gyromagnetic ratio, γ, is a constant for each nucleus (26,753 $s^{-1}gauss^{-1}$ for H).
- In a 14,092 gauss field, a 60 MHz photon is required to flip a proton.
- Low energy, radio frequency. =>

Magnetic Shielding

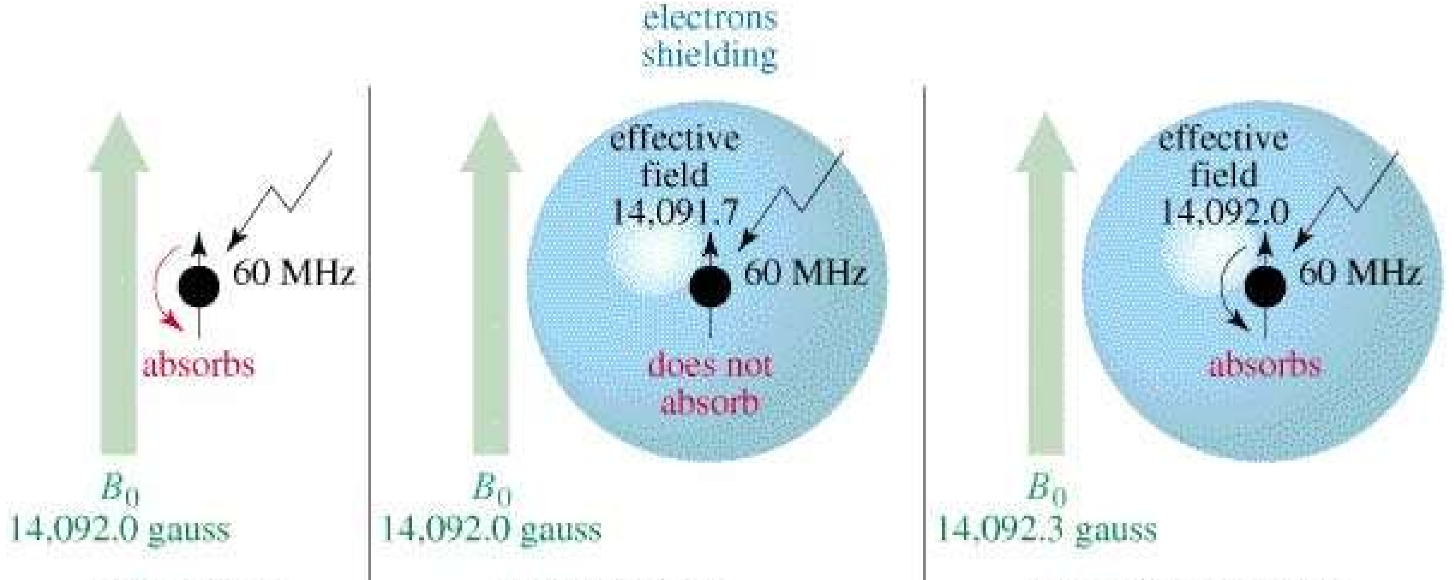


- If all protons absorbed the same amount of energy in a given magnetic field, not much information could be obtained.
- But protons are surrounded by electrons that shield them from the external field.
- Circulating electrons create an induced magnetic field that opposes the external magnetic field. =>

Shielded Protons



Magnetic field strength must be increased for a shielded proton to flip at the same frequency.



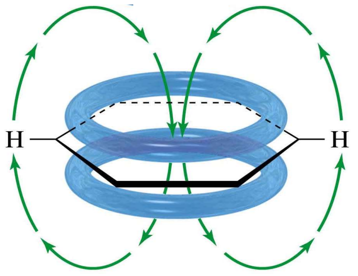
naked proton
absorbs at 14,092.0 G

shielded proton
feels less than 14,092.0 G

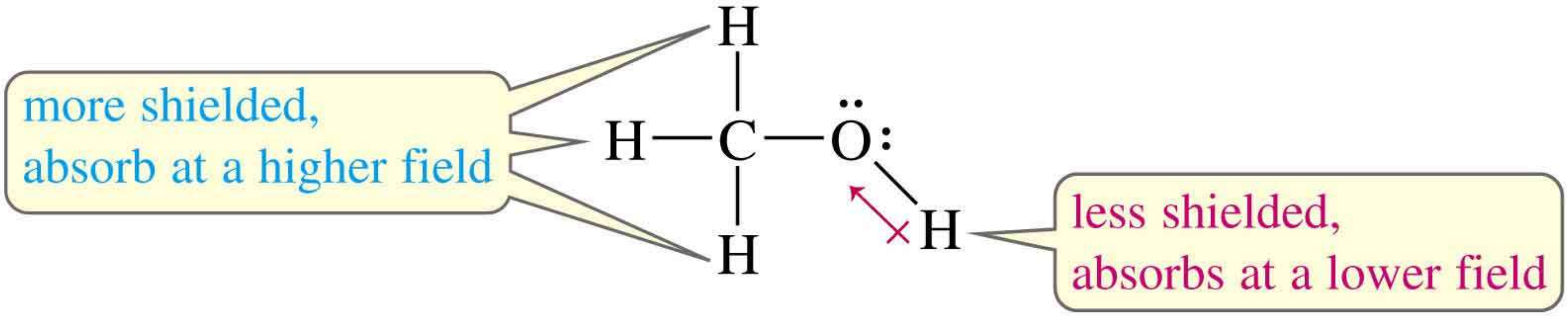
stronger applied field
compensates for shielding

=>

Protons in a Molecule



Depending on their chemical environment, protons in a molecule are shielded by different amounts.



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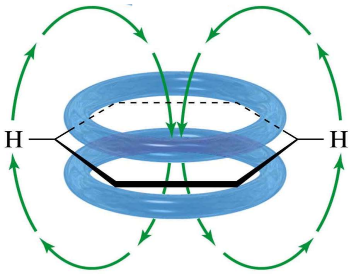
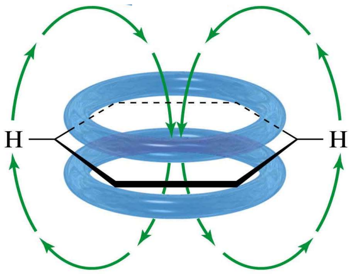
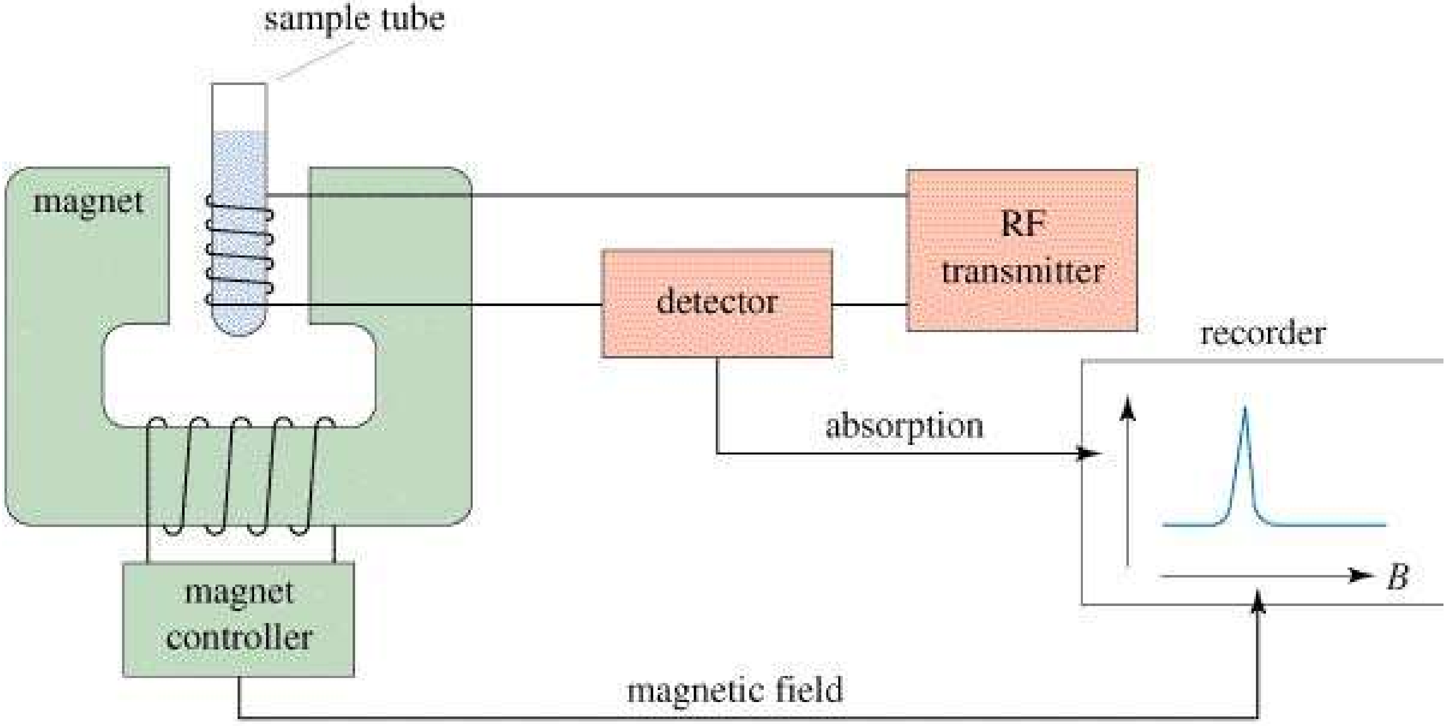


NMR Signals

- The ***number*** of signals shows how many different kinds of protons are present.
- The ***location*** of the signals shows how shielded or deshielded the proton is.
- The ***intensity*** of the signal shows the number of protons of that type.
- Signal ***splitting*** shows the number of protons on adjacent atoms. =>

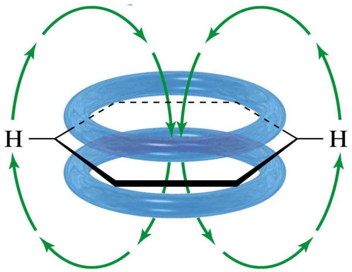
The NMR Spectrometer

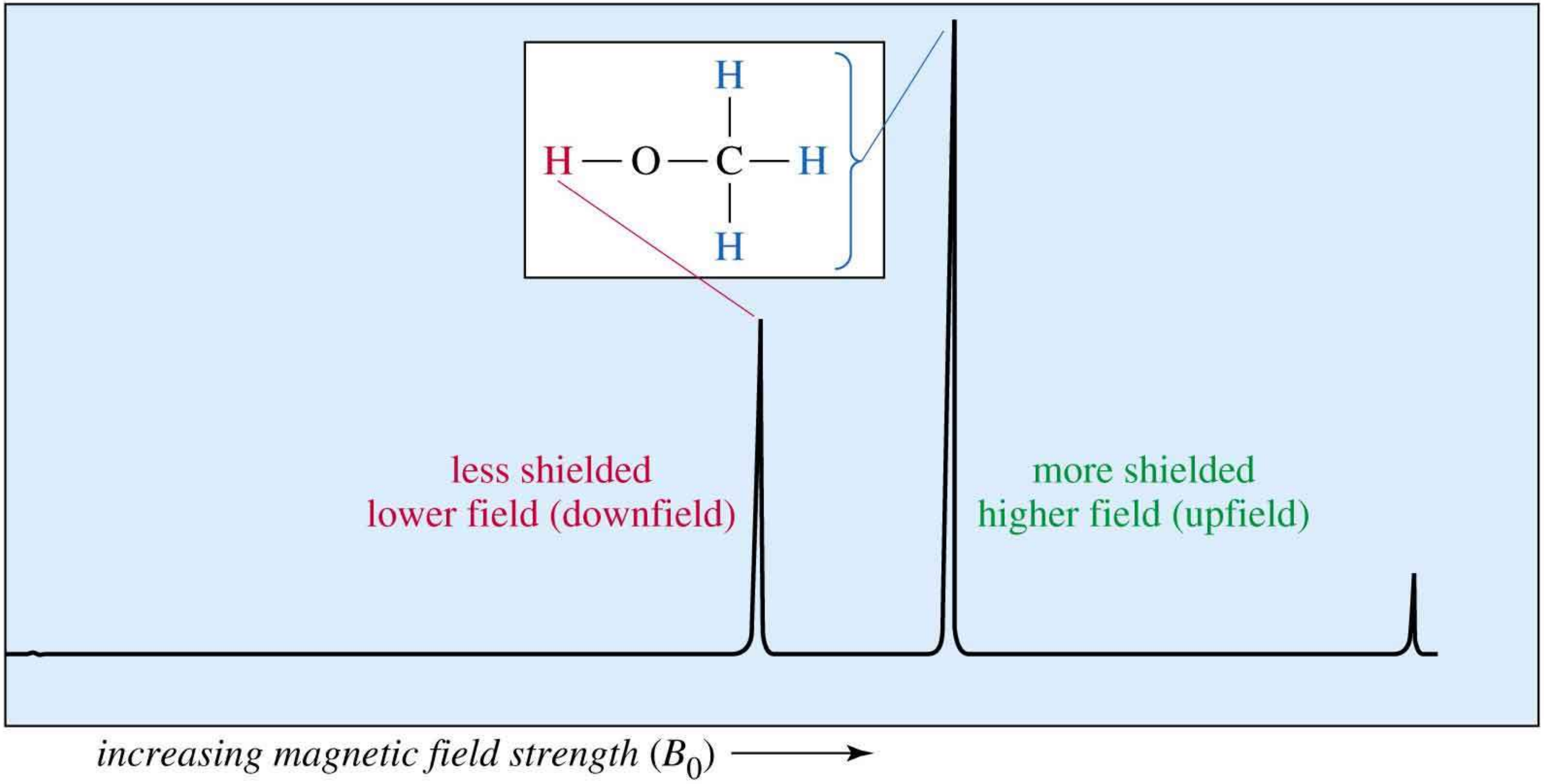




=>

The NMR Graph





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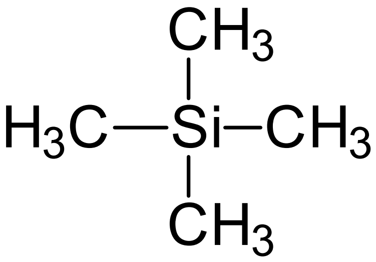
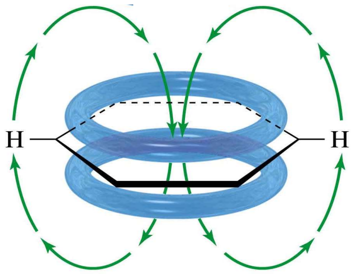


$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}-CH_3$$

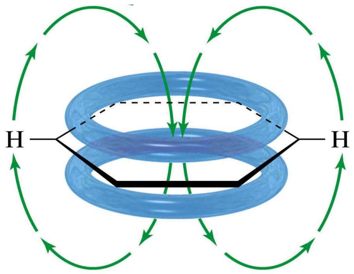
Tetramethylsilane



- TMS is added to the sample.
- Since silicon is less electronegative than carbon, TMS protons are highly shielded. Signal defined as zero.
- Organic protons absorb downfield (to the left) of the TMS signal.

=>

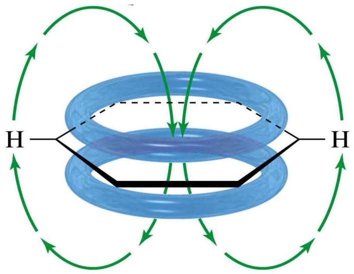
Chemical Shift



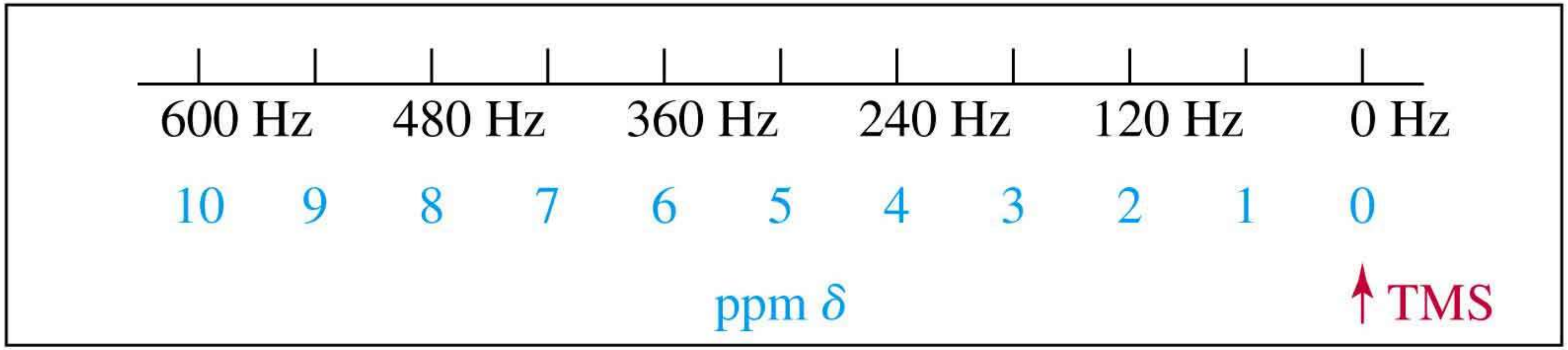
- Measured in parts per million.
- Ratio of shift downfield from TMS (Hz) to total spectrometer frequency (Hz).
- Same value for 60, 100, or 300 MHz machine.
- Called the delta scale.

=>

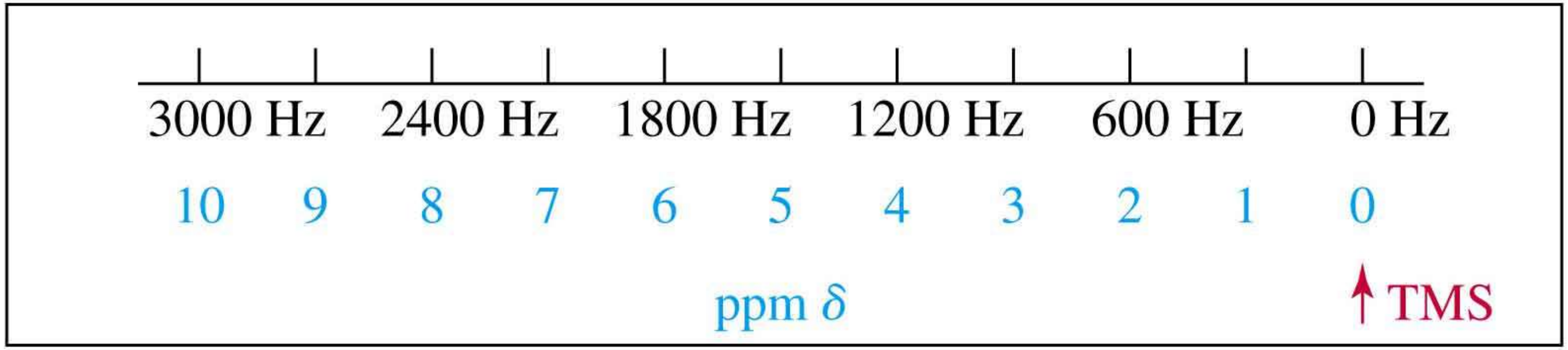
Delta Scale



$$\text{chemical shift, ppm } \delta = \frac{\text{shift downfield from TMS (in Hz)}}{\text{spectrometer frequency (in MHz)}}$$



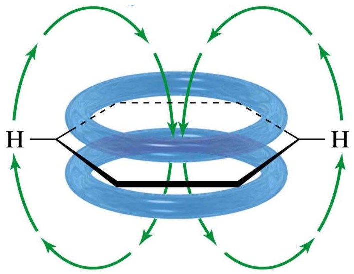
60 MHz



300 MHz

=>

Location of Signals



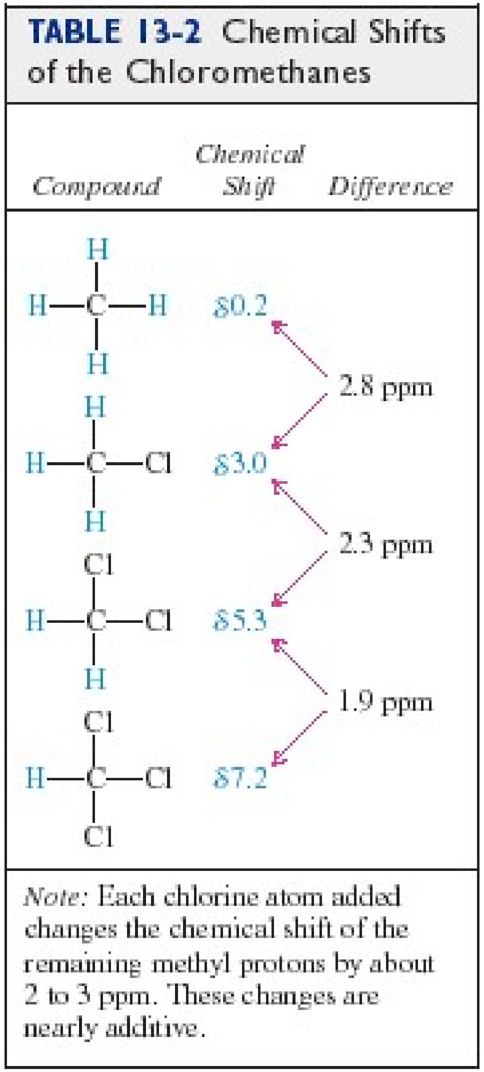


TABLE 13-2 Chemical Shifts of the Chloromethanes

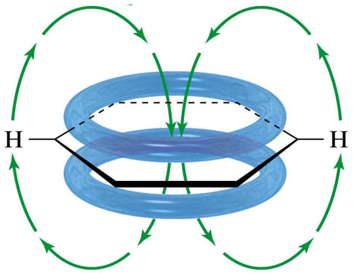
Compound	*Chemical Shift*	*Difference*
H H—C—H H	δ0.2	
		2.8 ppm
H H—C—Cl H	δ3.0	
		2.3 ppm
Cl H—C—Cl H	δ5.3	
		1.9 ppm
Cl H—C—Cl Cl	δ7.2	

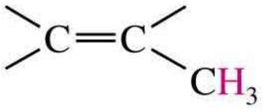
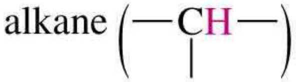
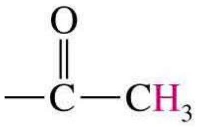
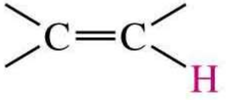
Note: Each chlorine atom added changes the chemical shift of the remaining methyl protons by about 2 to 3 ppm. These changes are nearly additive.

- More electronegative atoms deshield more and give larger shift values.
- Effect decreases with distance.
- Additional electronegative atoms cause increase in chemical shift.

=>

Typical Values

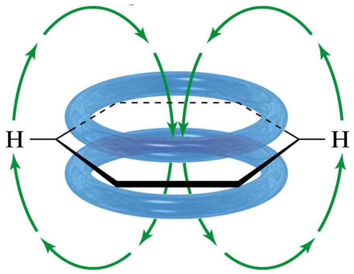


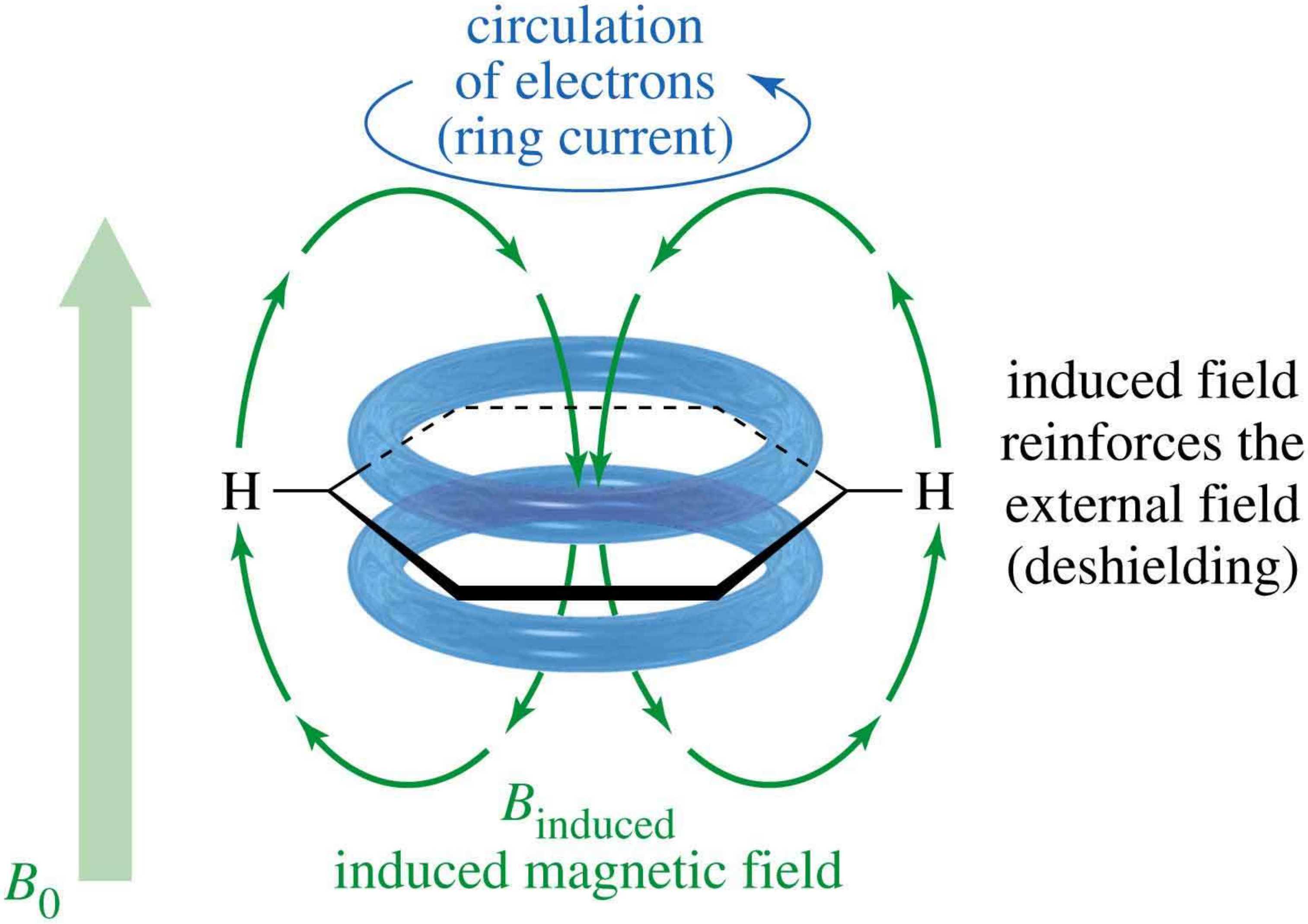
Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane ($-CH_3$)	0.9		1.7
alkane ($-CH_2-$)	1.3	$Ph-H$	7.2
alkane  $\left(-\underset{\vert}{C}H-\right)$	1.4	$Ph-CH_3$	2.3
 $-\overset{O}{\overset{\Vert}{C}}-CH_3$	2.1	$R-CHO$	9–10
$-C\equiv C-H$	2.5	$R-COOH$	10–12
$R-CH_2-X$ (X = halogen, O)	3–4	$R-OH$	variable, about 2–5
	5–6	$Ar-OH$	variable, about 4–7
		$R-NH_2$	variable, about 1.5–4

Note: These values are approximate, as all chemical shifts are affected by neighboring substituents. The numbers given here assume that alkyl groups are the only other substituents present. A more complete table of chemical shifts appears in Appendix 1.

=>

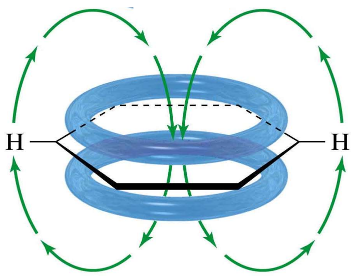
Aromatic Protons, δ7-δ8

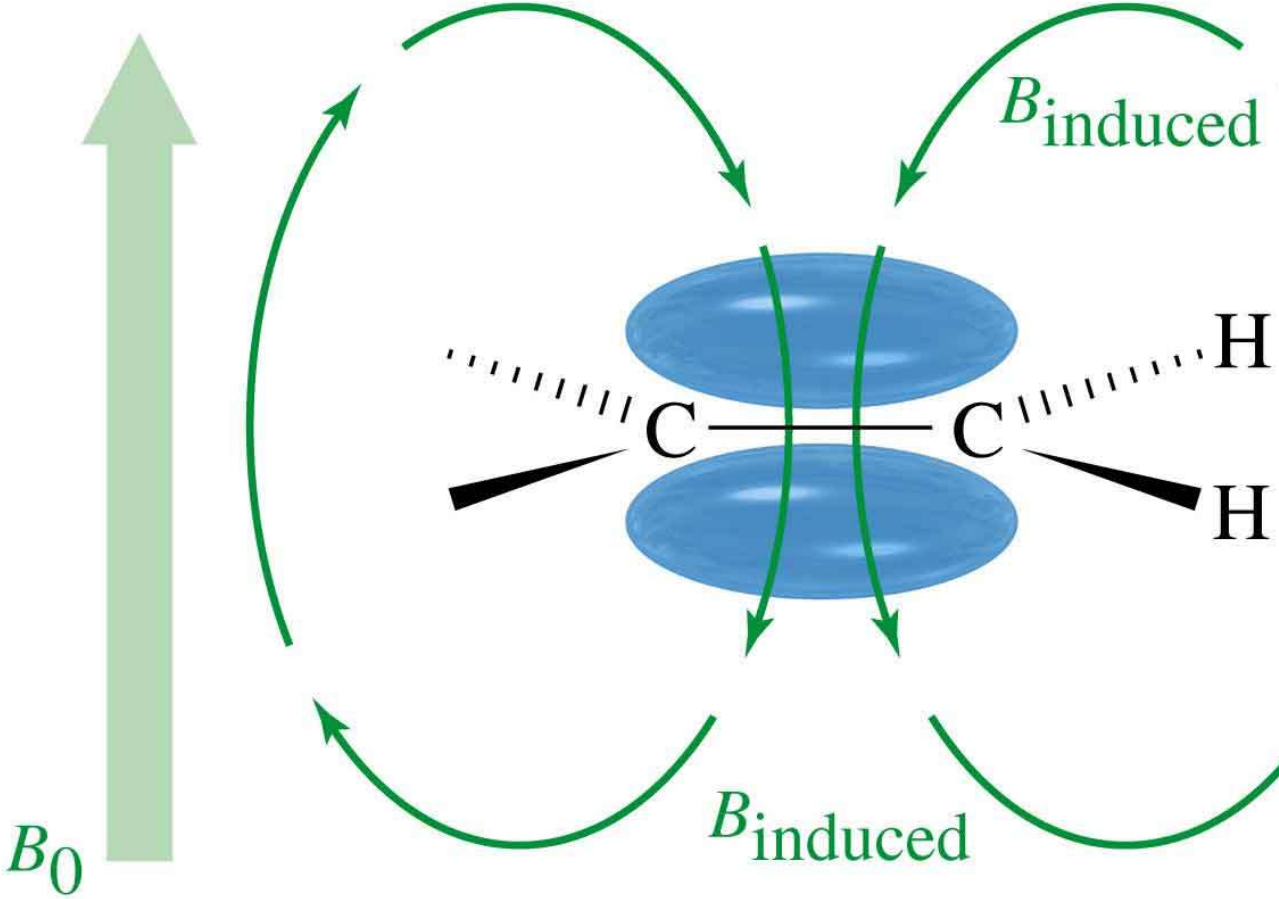




=>

Vinyl Protons, δ5-δ6

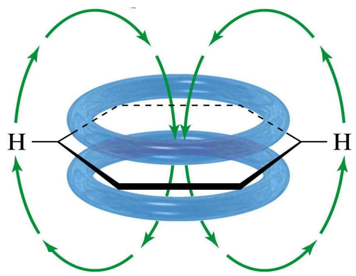


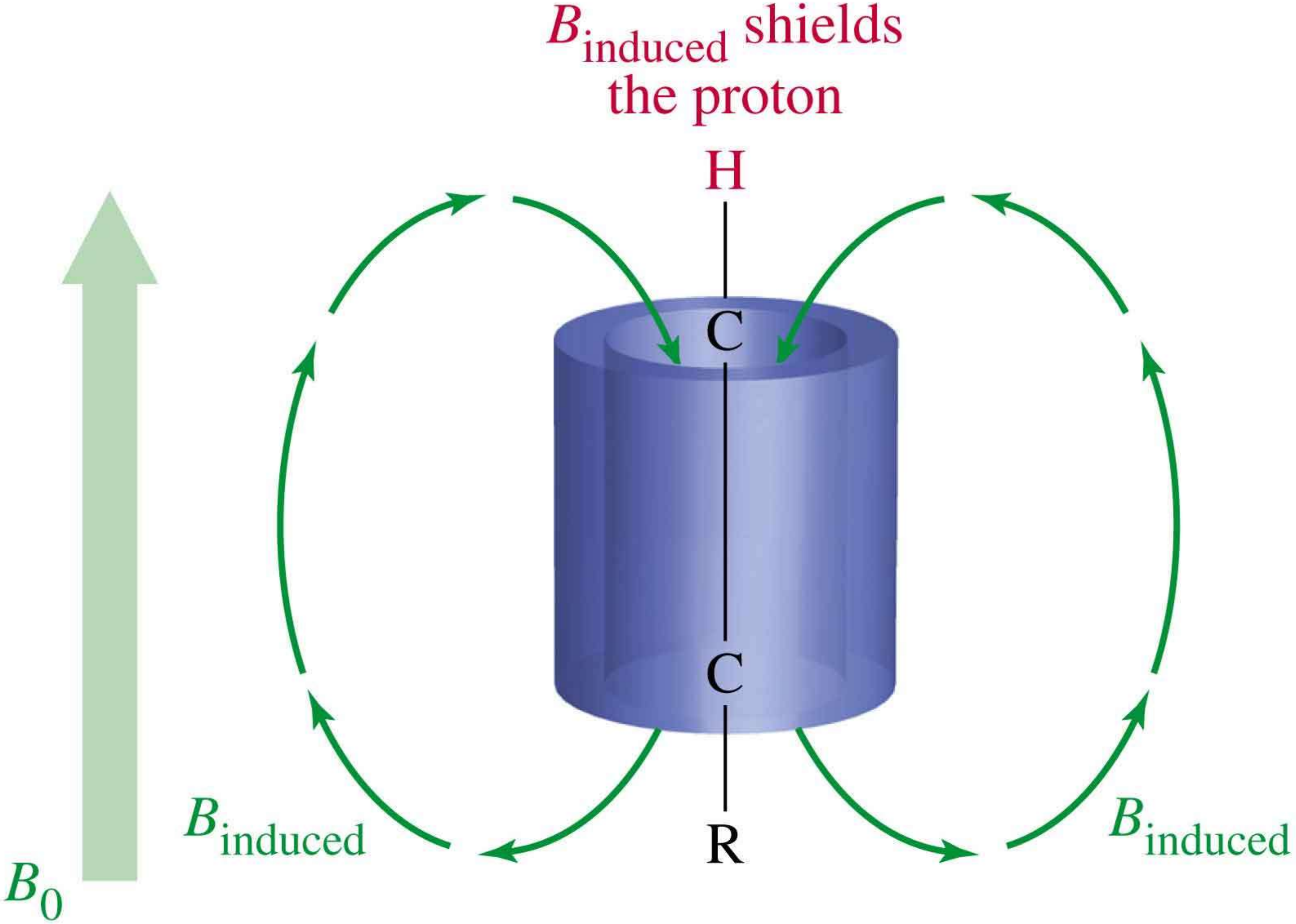


induced field
reinforces the
external field
(deshielding)

=>

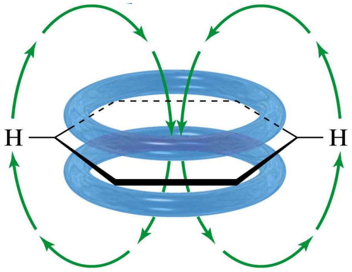
Acetylenic Protons, δ2.5

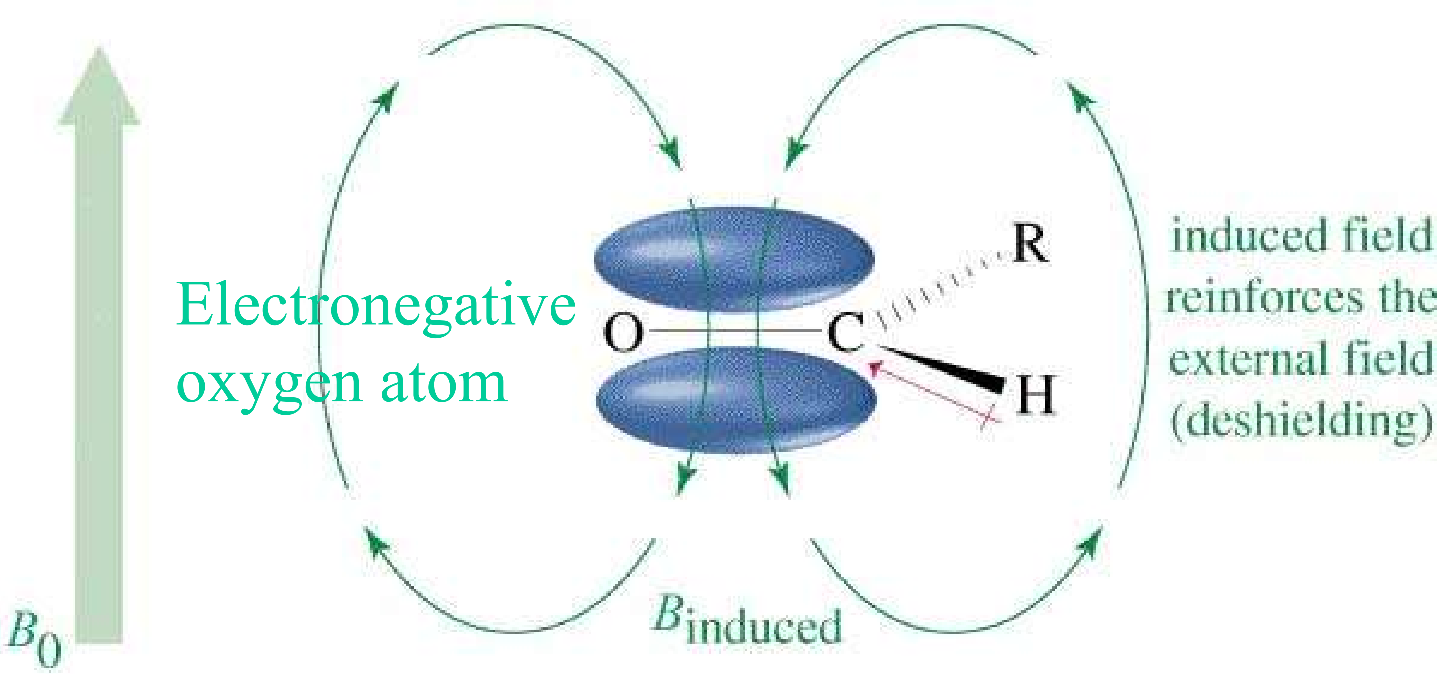




=>

Aldehyde Proton, δ9-δ10

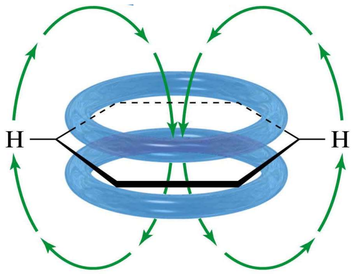




Electronegative oxygen atom

=>

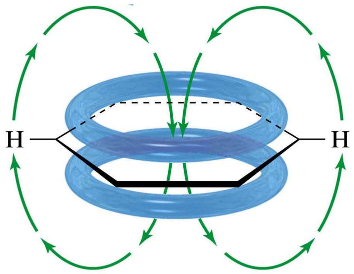
O-H and N-H Signals

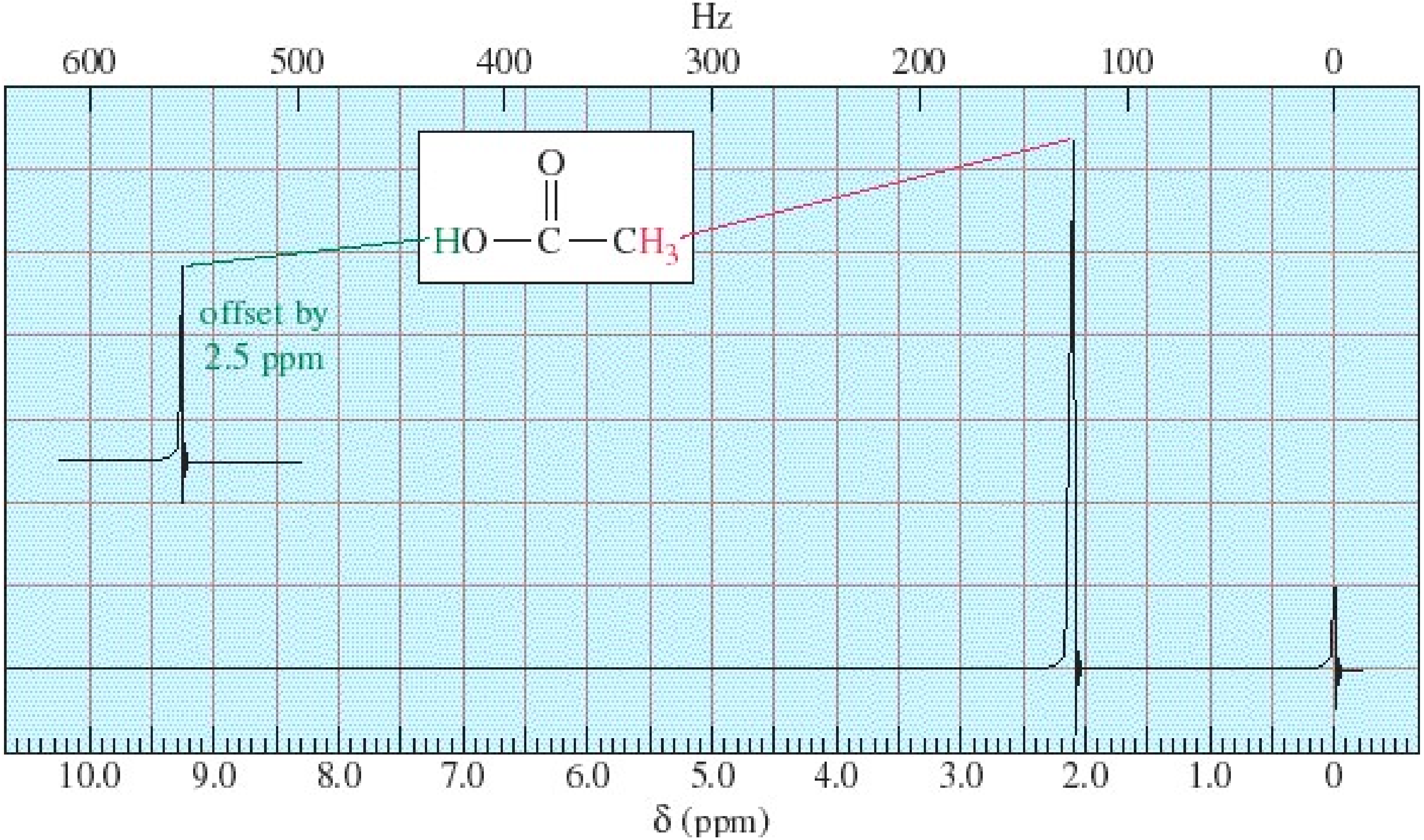


- Chemical shift depends on concentration.
- Hydrogen bonding in concentrated solutions deshield the protons, so signal is around δ3.5 for N-H and δ4.5 for O-H.
- Proton exchanges between the molecules broaden the peak.

=>

Carboxylic Acid Proton, δ10+





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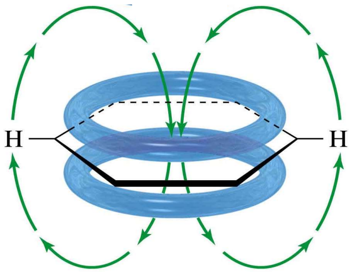
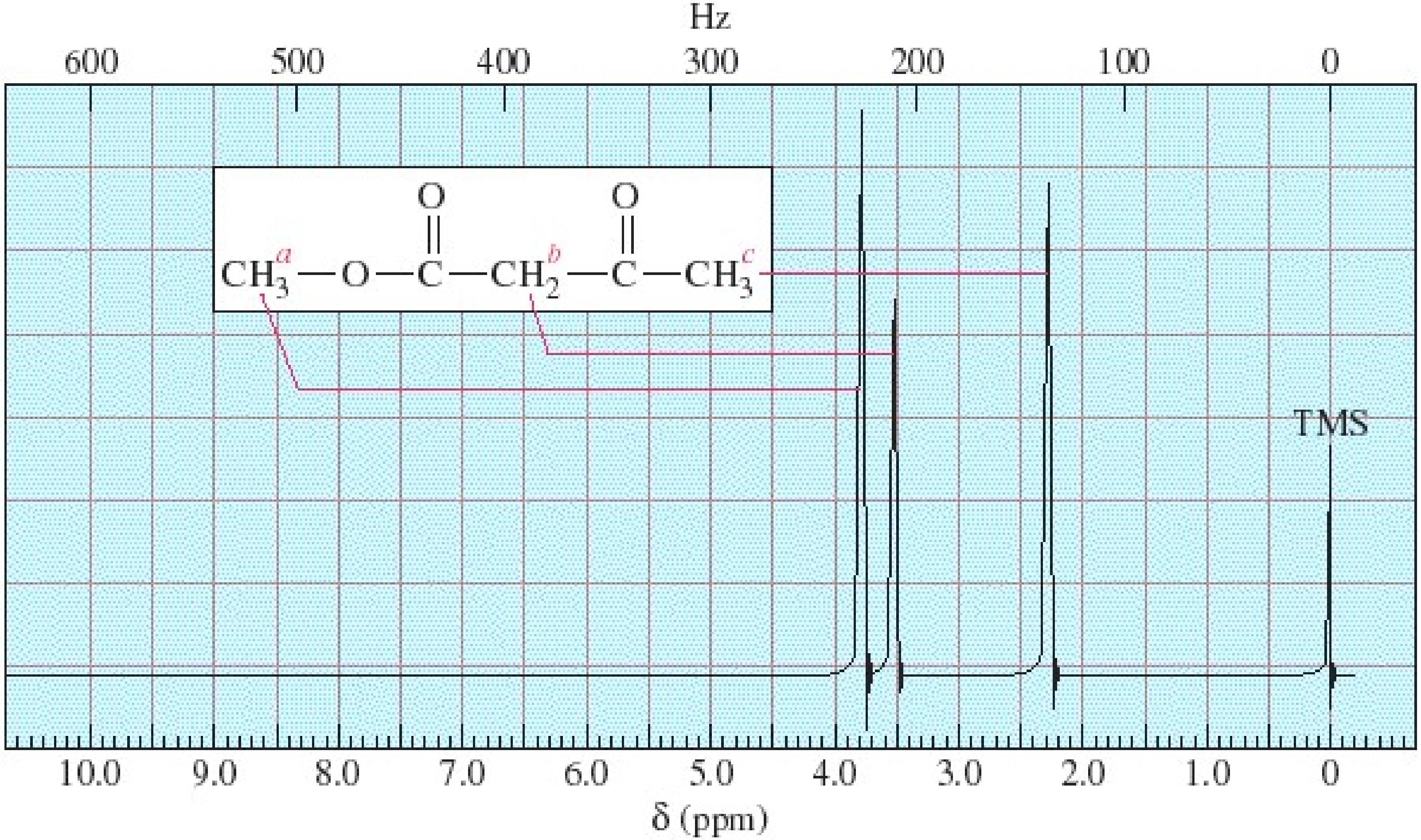


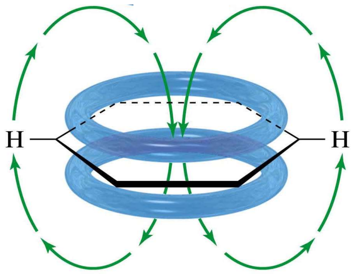
Number of Signals

Equivalent hydrogens have the same chemical shift.

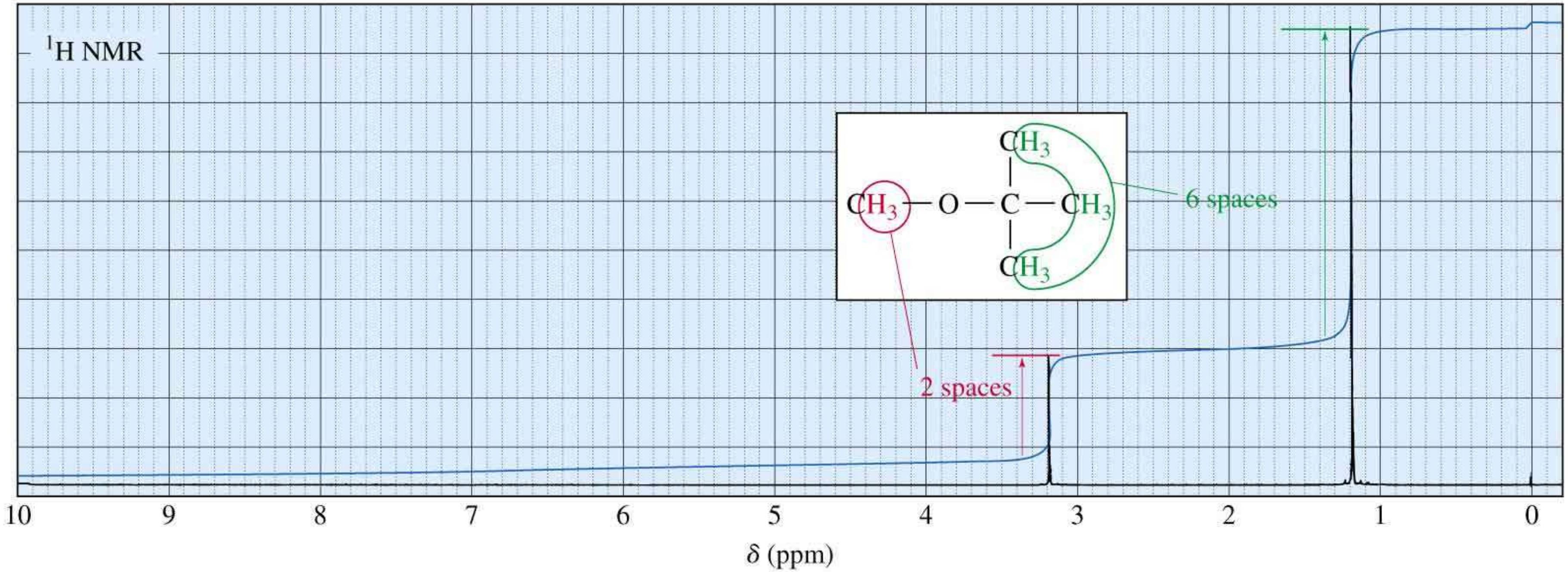


=>

Intensity of Signals



- The area under each peak is proportional to the number of protons.
- Shown by integral trace.



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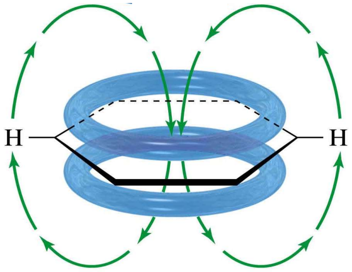
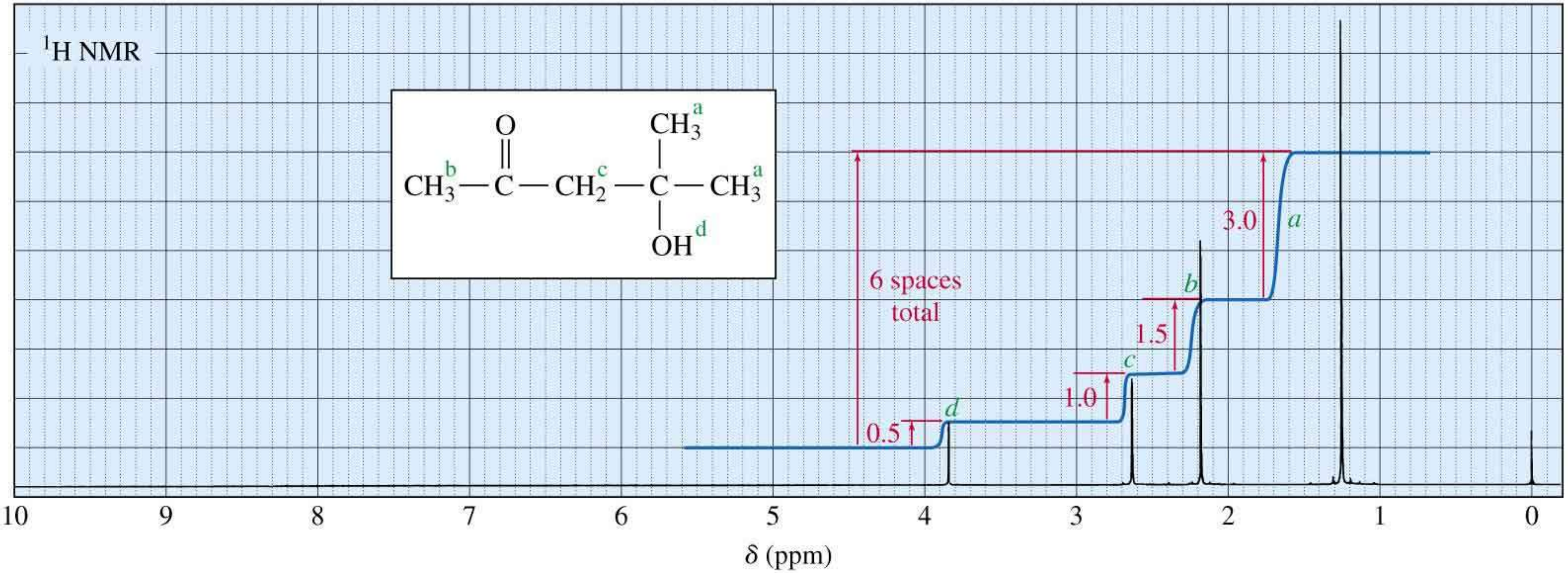
How Many Hydrogens?

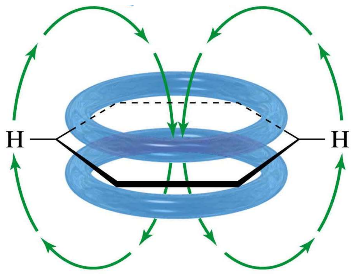


When the molecular formula is known, each integral rise can be assigned to a particular number of hydrogens.



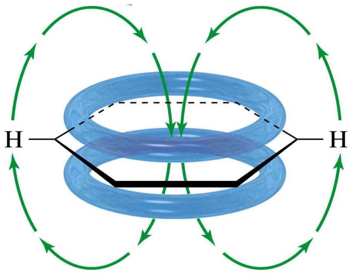
=>

Spin-Spin Splitting

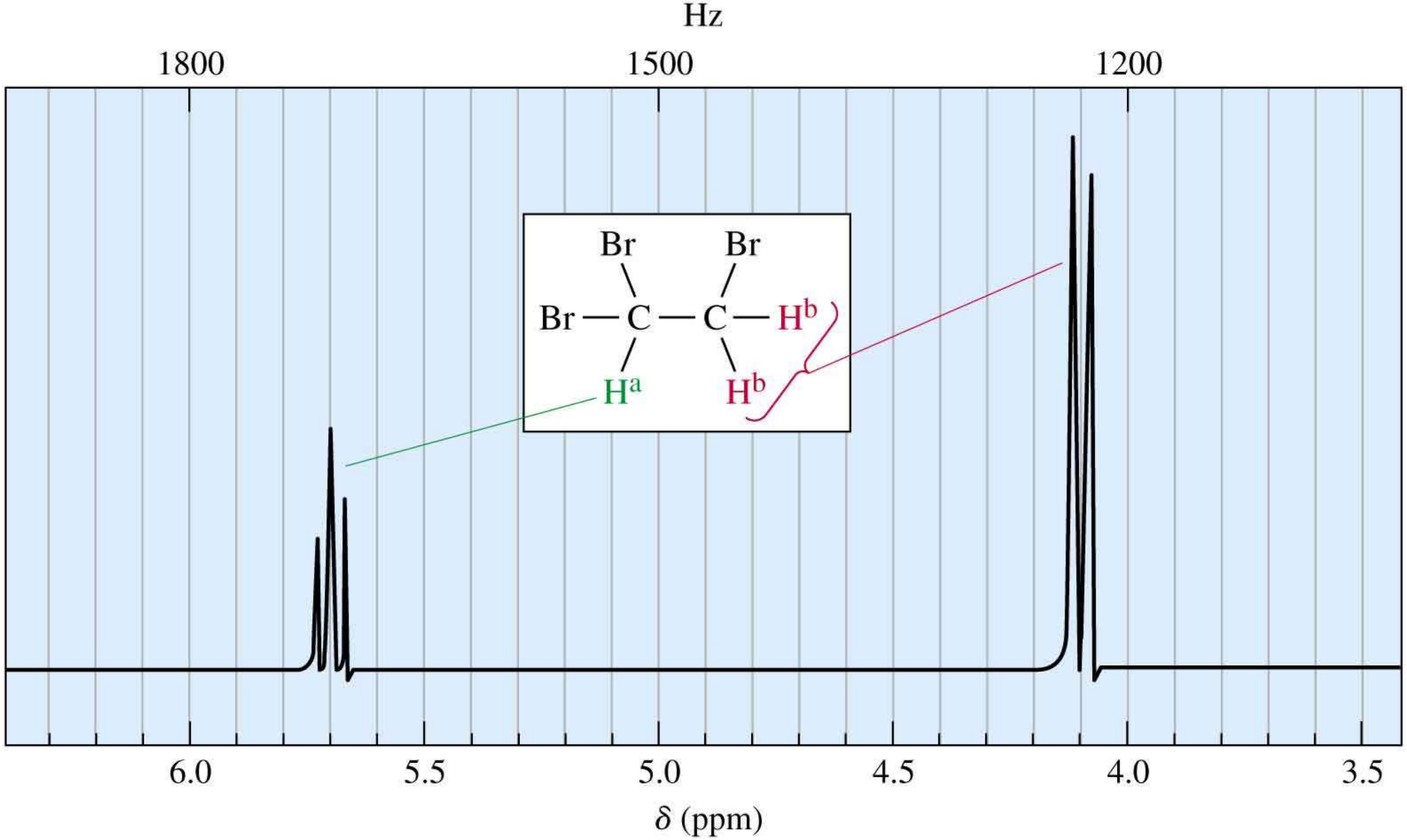


- Nonequivalent protons on adjacent carbons have magnetic fields that may align with or oppose the external field.
- This magnetic coupling causes the proton to absorb slightly downfield when the external field is reinforced and slightly upfield when the external field is opposed.
- All possibilities exist, so signal is split. =>

1,1,2-Tribromoethane

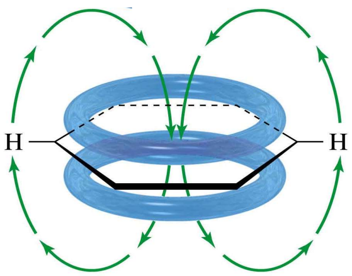


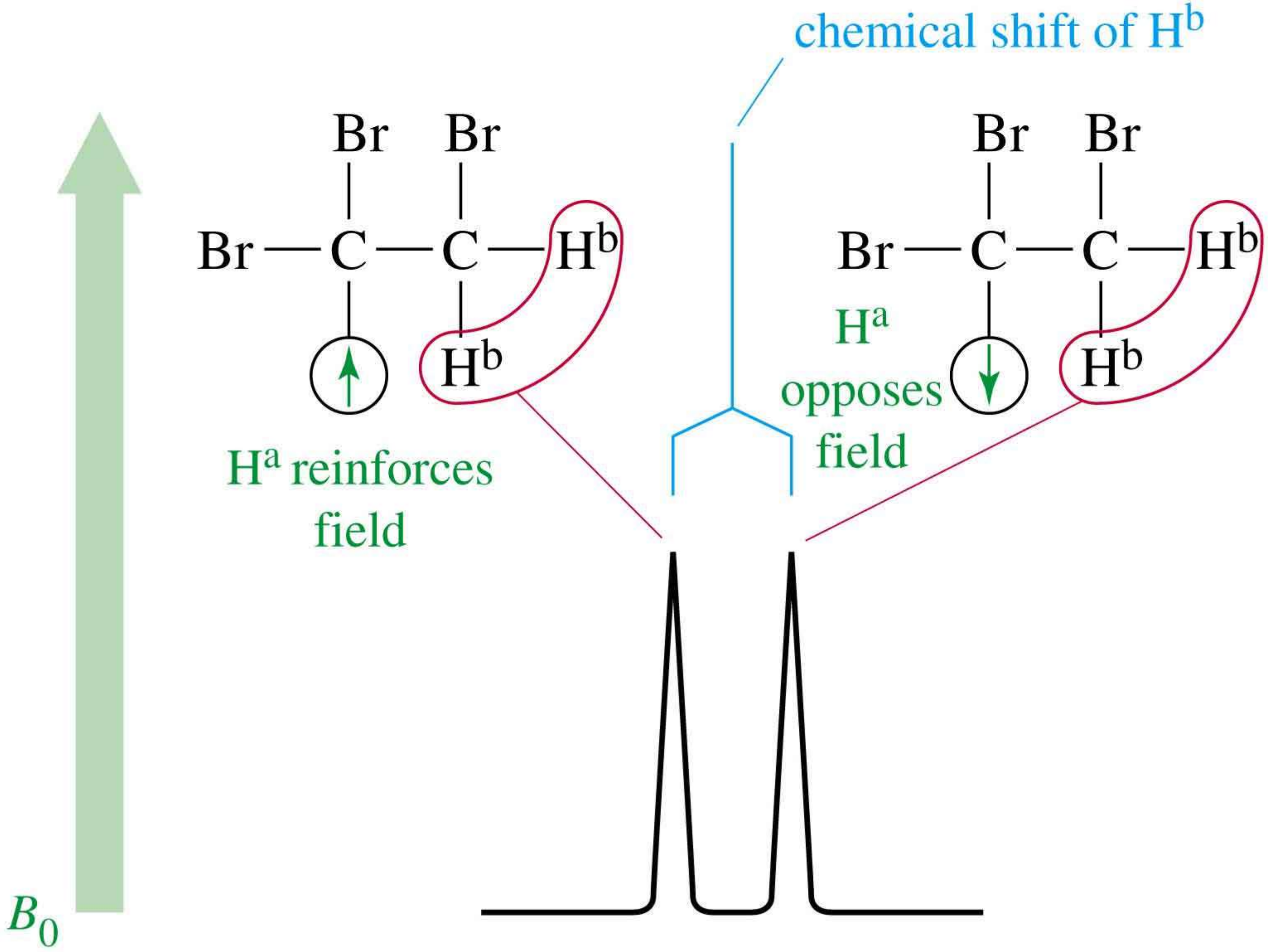
Nonequivalent protons on adjacent carbons.



=>

Doublet: 1 Adjacent Proton




chemical shift of H^b

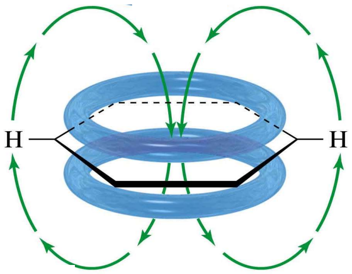
H^a reinforces field

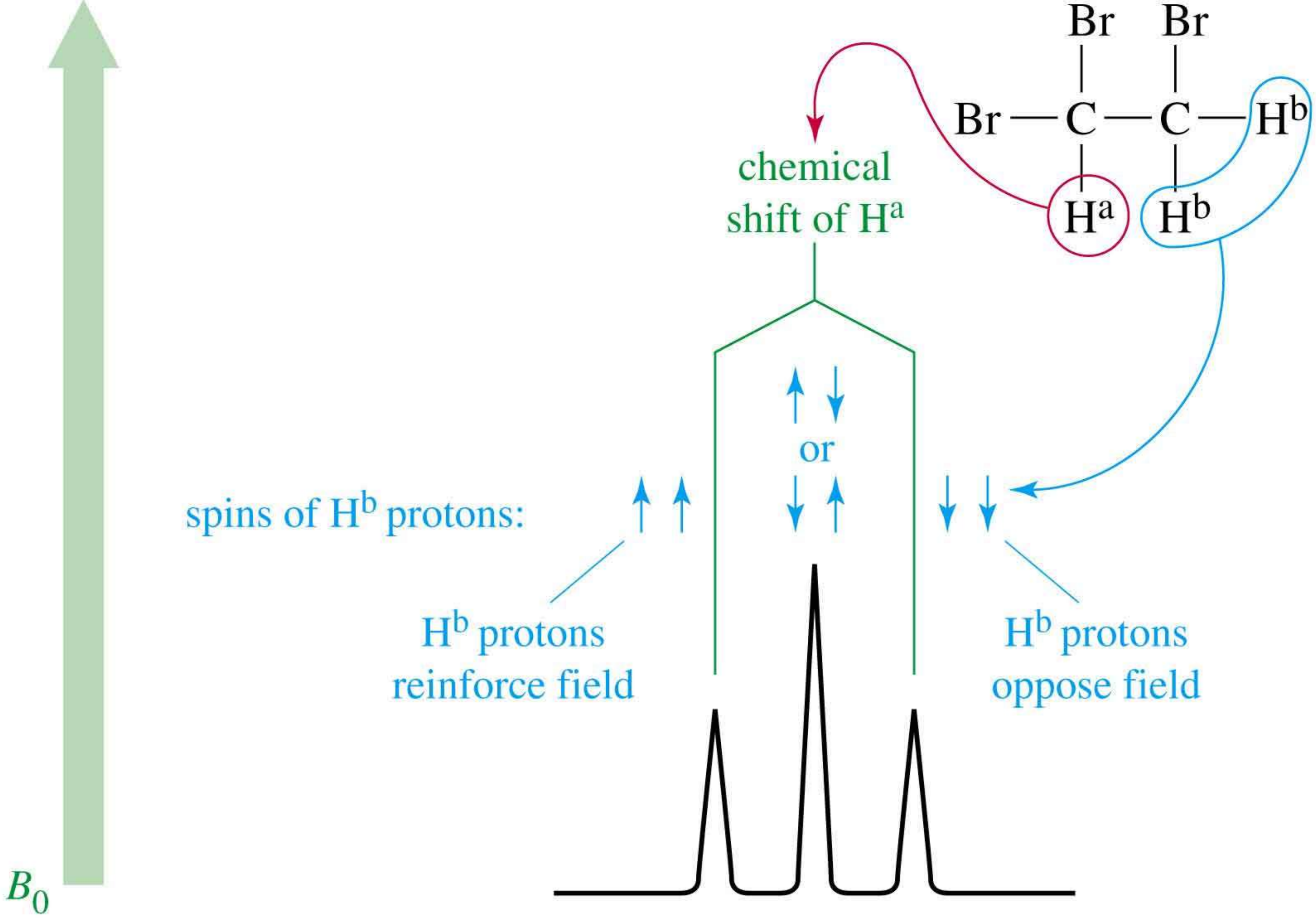
H^a opposes field

B_0

=>

Triplet: 2 Adjacent Protons





chemical shift of H^a

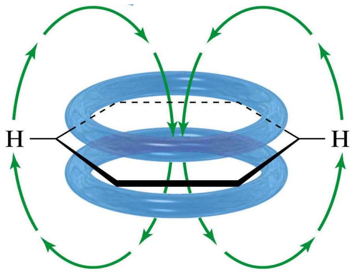
spins of H^b protons: ↑↑ ↑↓ or ↓↑ ↓↓

H^b protons reinforce field

H^b protons oppose field

=>

The *N* + 1 Rule



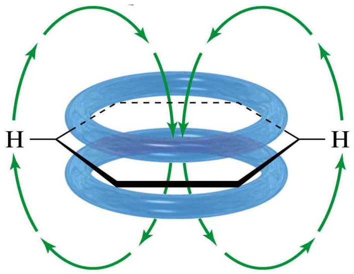
If a signal is split by *N* equivalent protons, it is split into *N* + 1 peaks.

Relative Peak Intensities of Symmetric Multiplets

Number of Equivalent Protons Causing Splitting	*Number of Peaks (multiplicity)*	*Area Ratios (Pascal's triangle)*
0	1 (singlet)	1
1	2(doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

=>

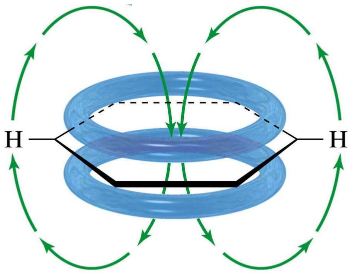
Range of Magnetic Coupling

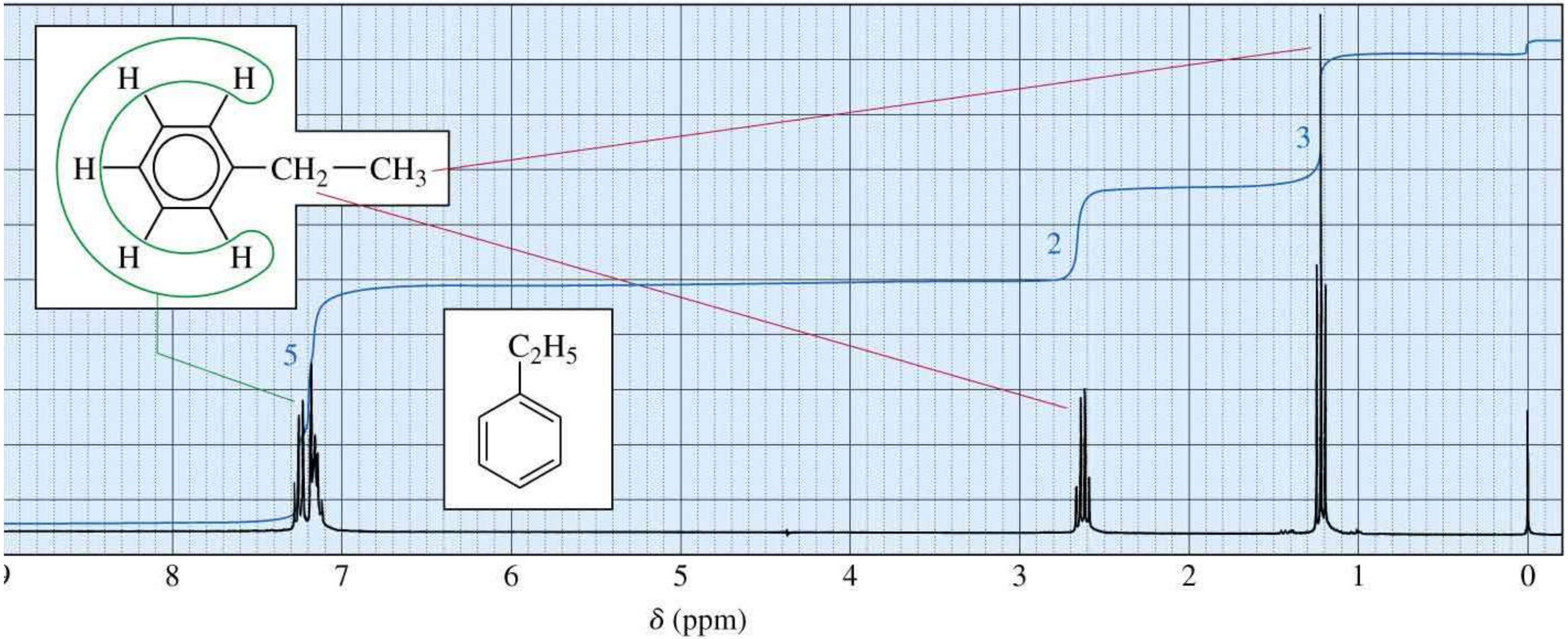


- Equivalent protons do not split each other.
- Protons bonded to the same carbon will split each other <u>only</u> if they are not equivalent.
- Protons on adjacent carbons normally will couple.
- Protons separated by four or more bonds will not couple.

=>

Splitting for Ethyl Groups





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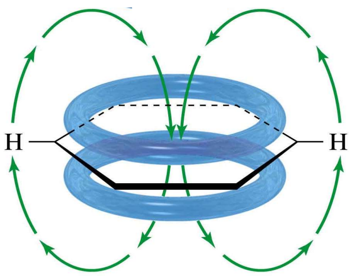
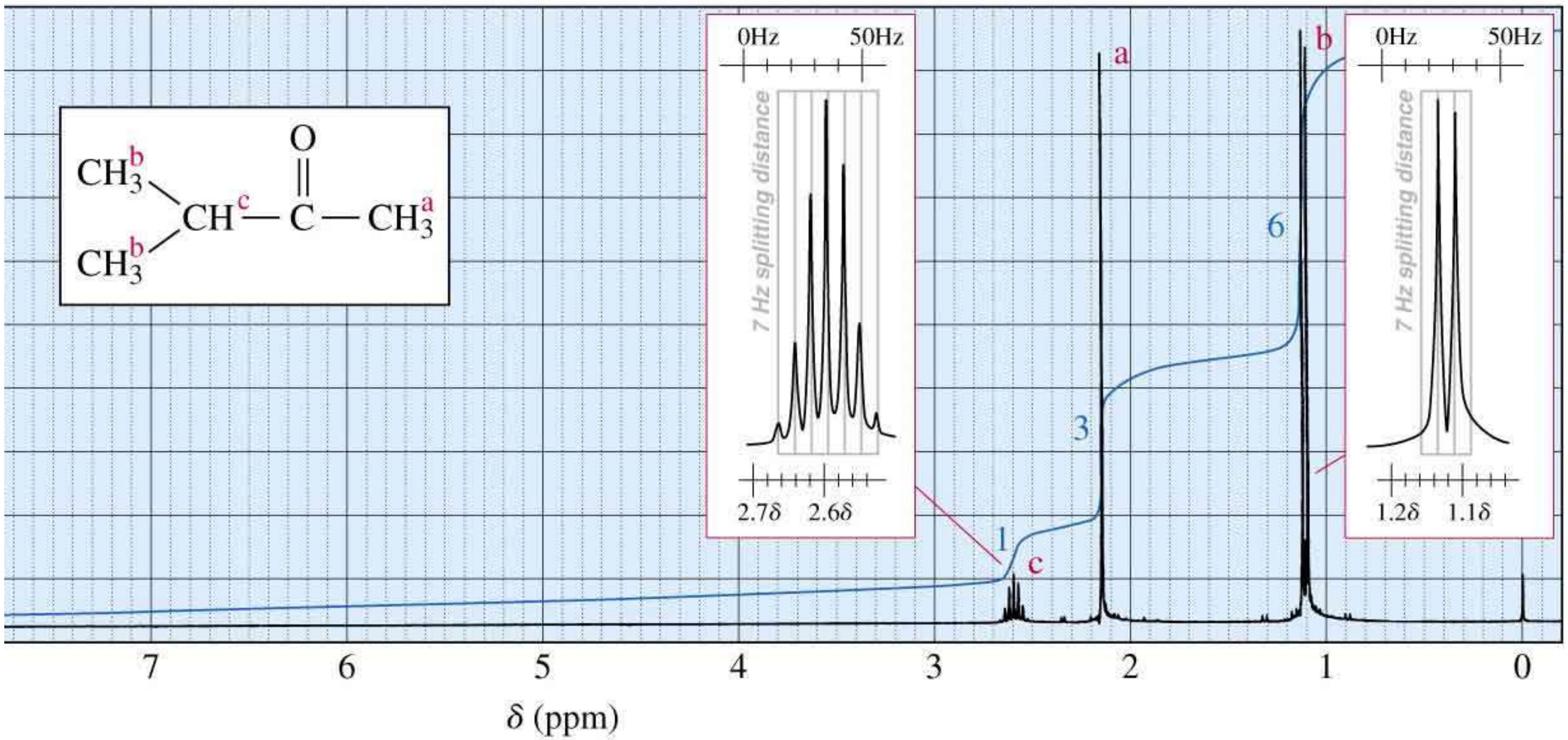
Splitting for Isopropyl Groups





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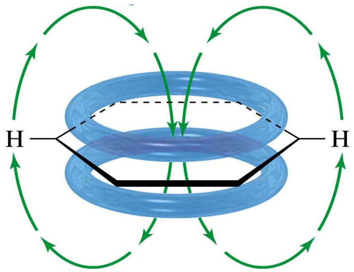
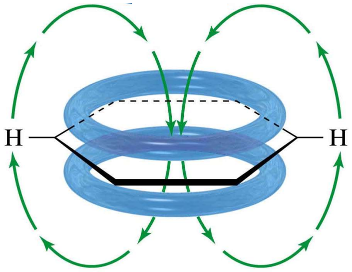


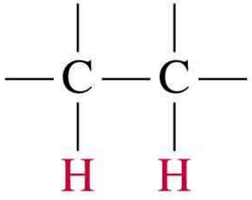
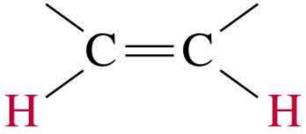
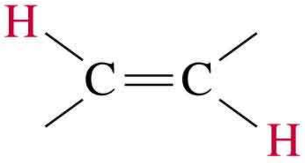
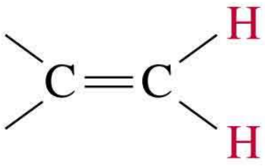
Coupling Constants

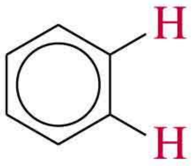
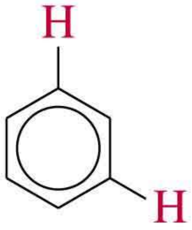
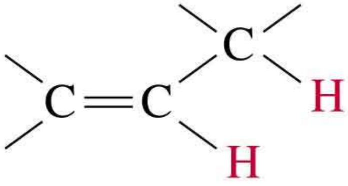
- Distance between the peaks of multiplet
- Measured in Hz
- Not dependent on strength of the external field
- Multiplets with the same coupling constants may come from adjacent groups of protons that split each other.

=>

Values for Coupling Constants

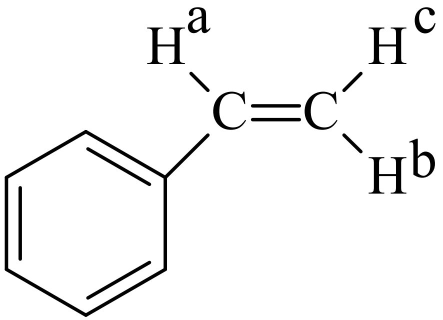


		Approx. *J*
	(free rotation)	7 Hz[a]
	(cis)	10 Hz
	(trans)	15 Hz
	(geminal)	2 Hz

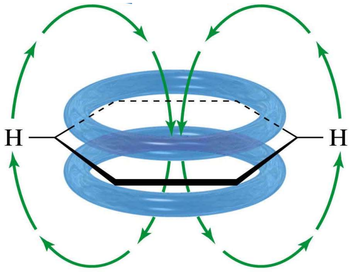
	Approx. *J*
 (ortho)	8 Hz
 (meta)	2 Hz
 (allylic)	6 Hz

=>

[a] The value of 7 Hz in an alkyl group is averaged for rapid rotation about the carbon–carbon bond. If rotation is hindered by a ring or bulky groups, other splitting constants may be observed.



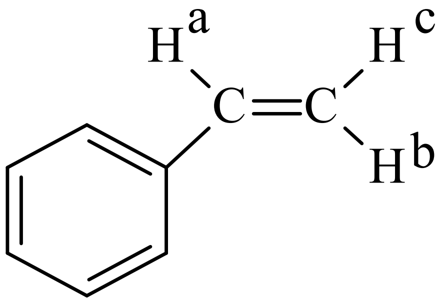
Complex Splitting

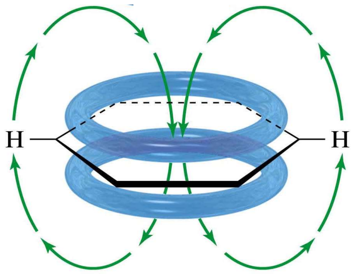


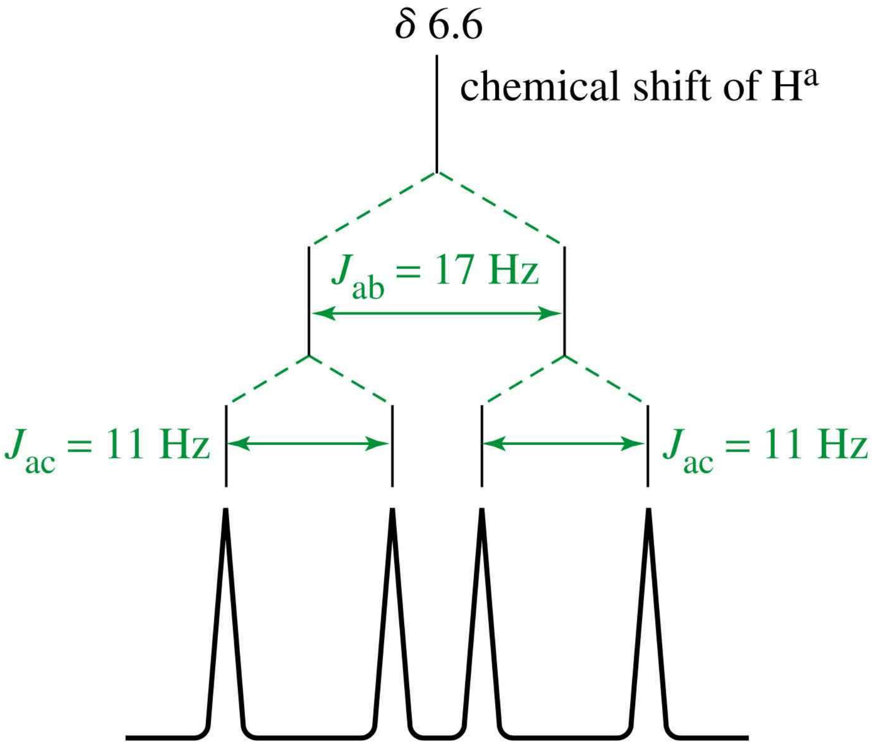
- Signals may be split by adjacent protons, different from each other, with different coupling constants.
- Example: H^a of styrene which is split by an adjacent H *trans* to it (J = 17 Hz) and an adjacent H *cis* to it (J = 11 Hz).

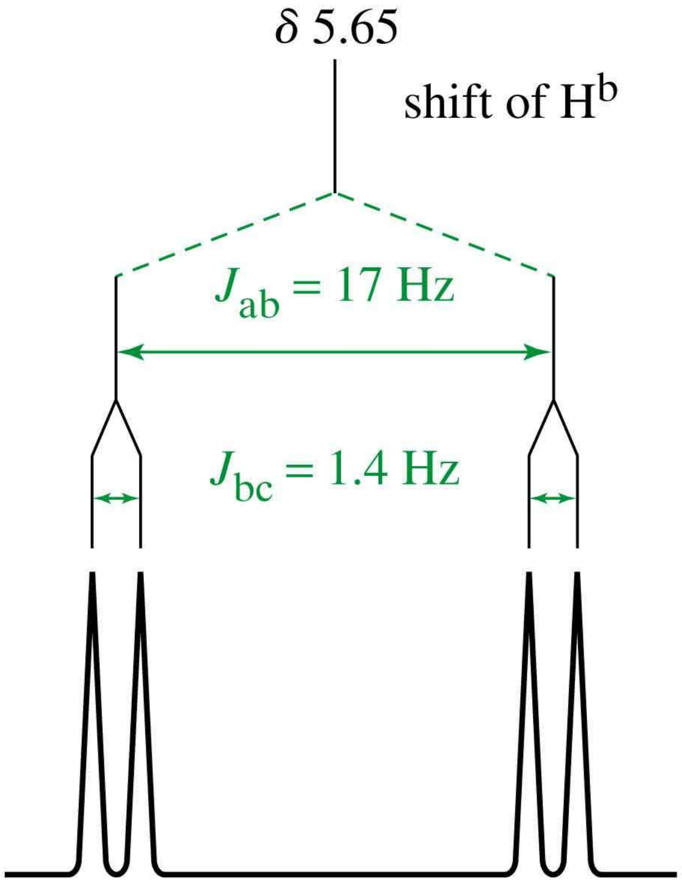
=>

Splitting Tree









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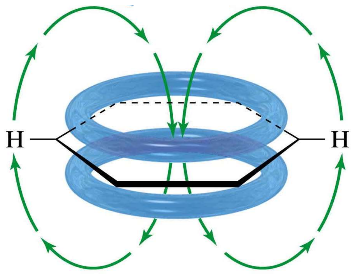
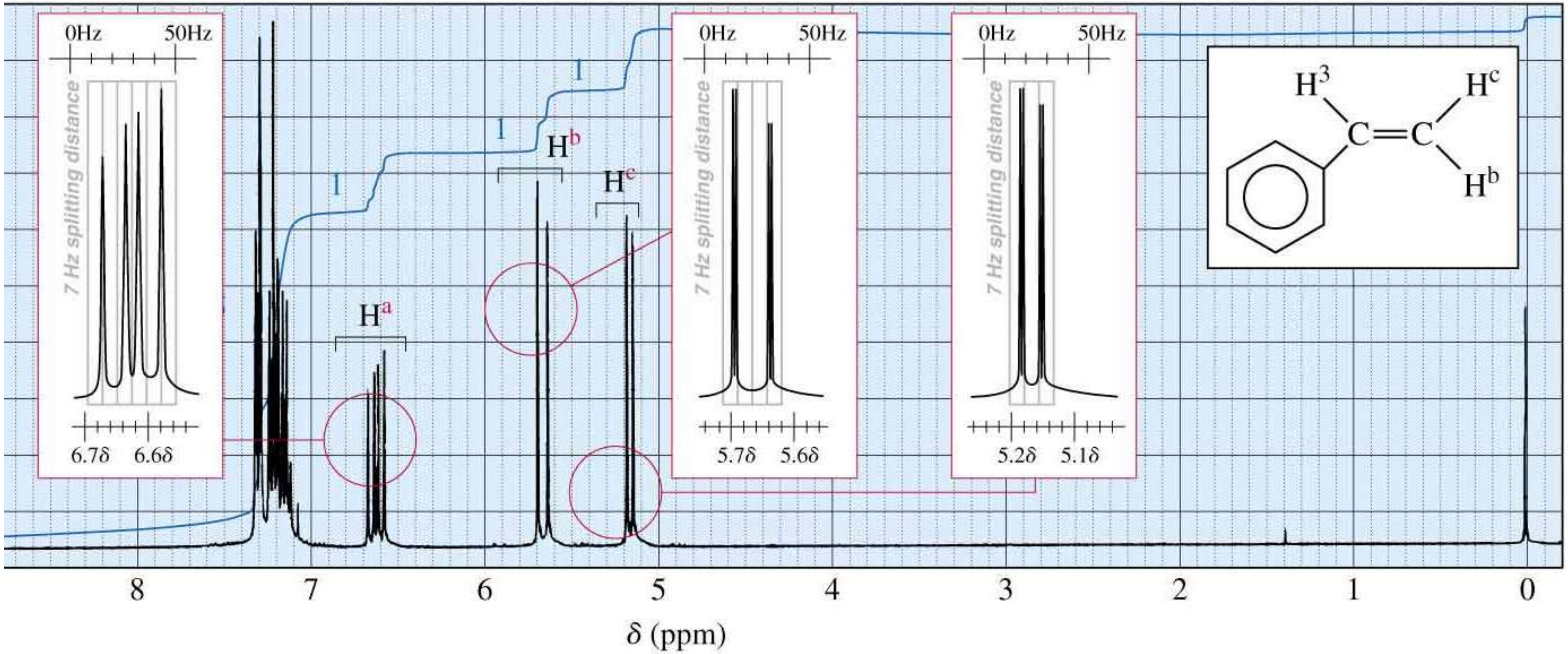
Spectrum for Styrene





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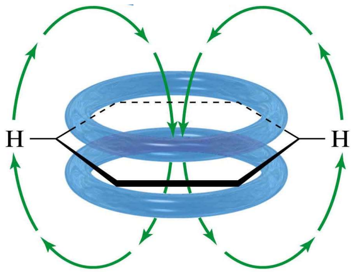
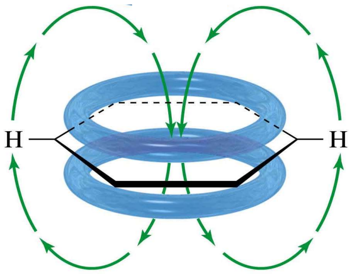
Stereochemical Nonequivalence

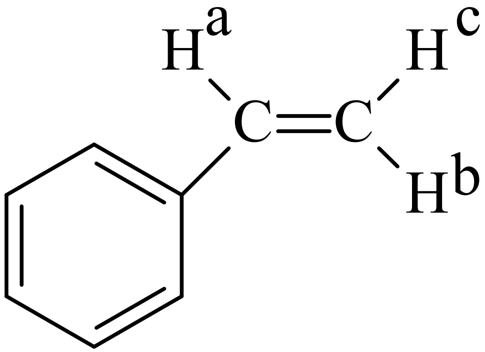


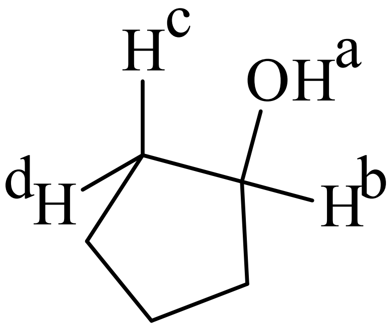
- Usually, two protons on the same C are equivalent and do not split each other.
- If the replacement of each of the protons of a -CH_2 group with an imaginary "Z" gives stereoisomers, then the protons are non-equivalent and will split each other.

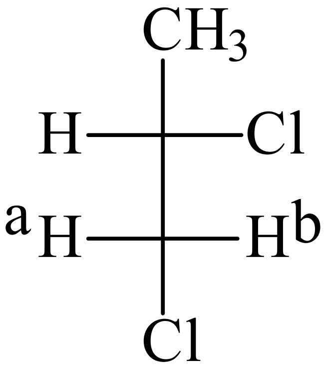
=>

Some Nonequivalent Protons









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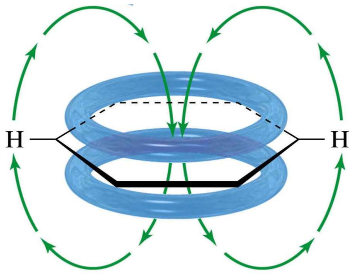
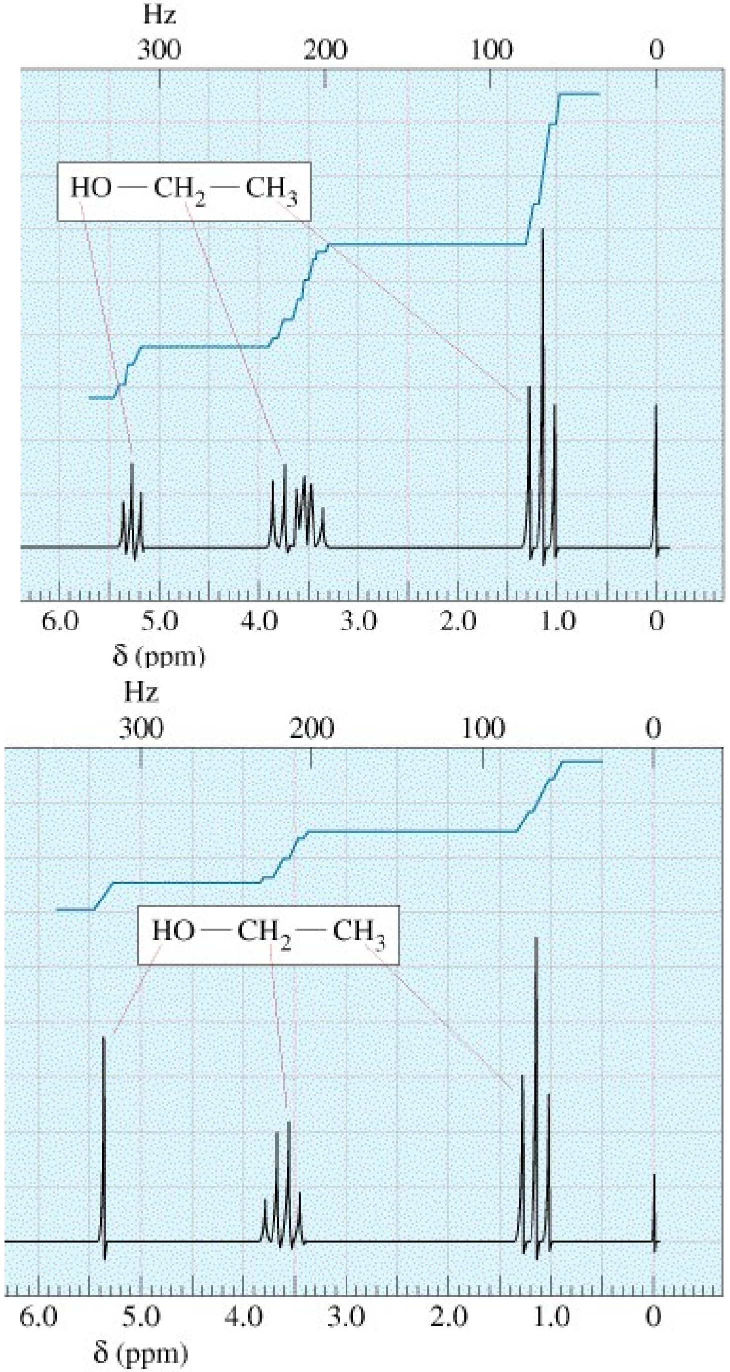
Time Dependence

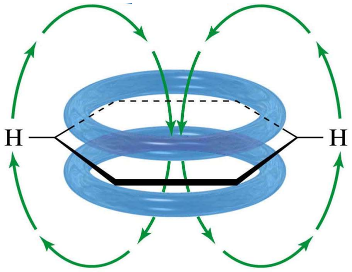


- Molecules are tumbling relative to the magnetic field, so NMR is an averaged spectrum of all the orientations.
- Axial and equatorial protons on cyclohexane interconvert so rapidly that they give a single signal.
- Proton transfers for OH and NH may occur so quickly that the proton is not split by adjacent protons in the molecule.

=>

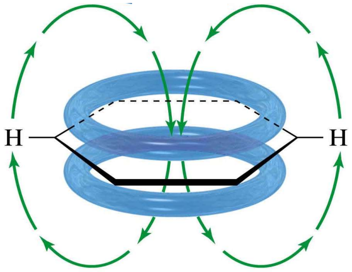


Hydroxyl Proton



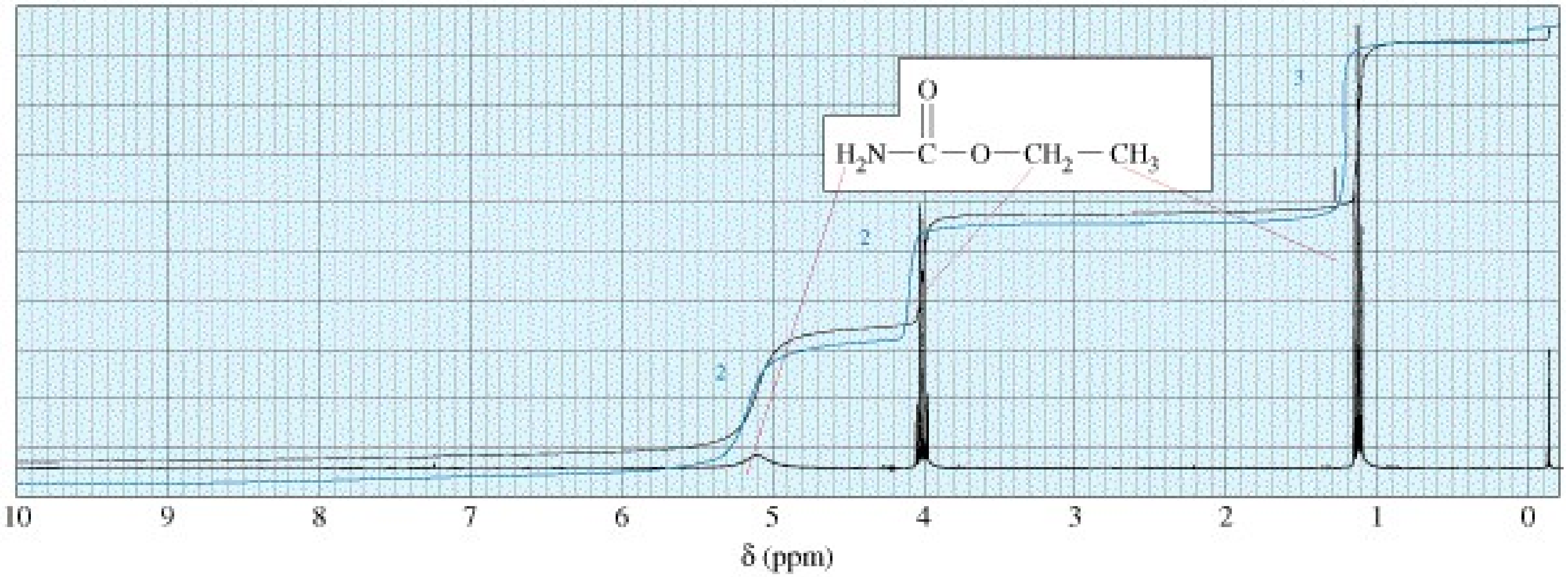
- Ultrapure samples of ethanol show splitting.
- Ethanol with a small amount of acidic or basic impurities will not show splitting.

=>



N-H Proton

- Moderate rate of exchange.
- Peak may be broad.



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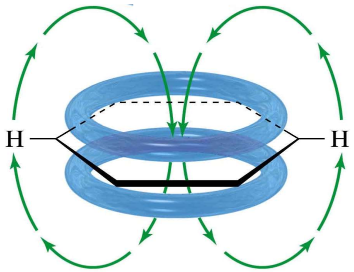
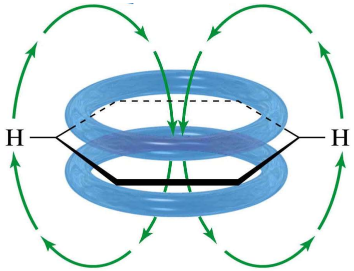
Identifying the O-H or N-H Peak



- Chemical shift will depend on concentration and solvent.
- To verify that a particular peak is due to O-H or N-H, shake the sample with D_2O
- Deuterium will exchange with the O-H or N-H protons.
- On a second NMR spectrum the peak will be absent, or much less intense.

=>

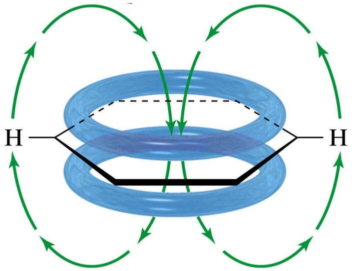
Carbon-13



- ^{12}C has no magnetic spin.
- ^{13}C has a magnetic spin, but is only 1% of the carbon in a sample.
- The gyromagnetic ratio of ^{13}C is one-fourth of that of ^{1}H.
- Signals are weak, getting lost in noise.
- Hundreds of spectra are taken, averaged.

=>

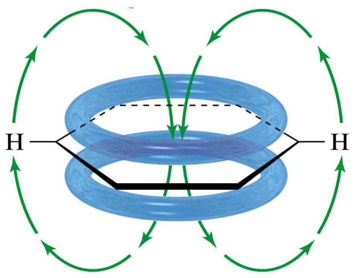
Fourier Transform NMR

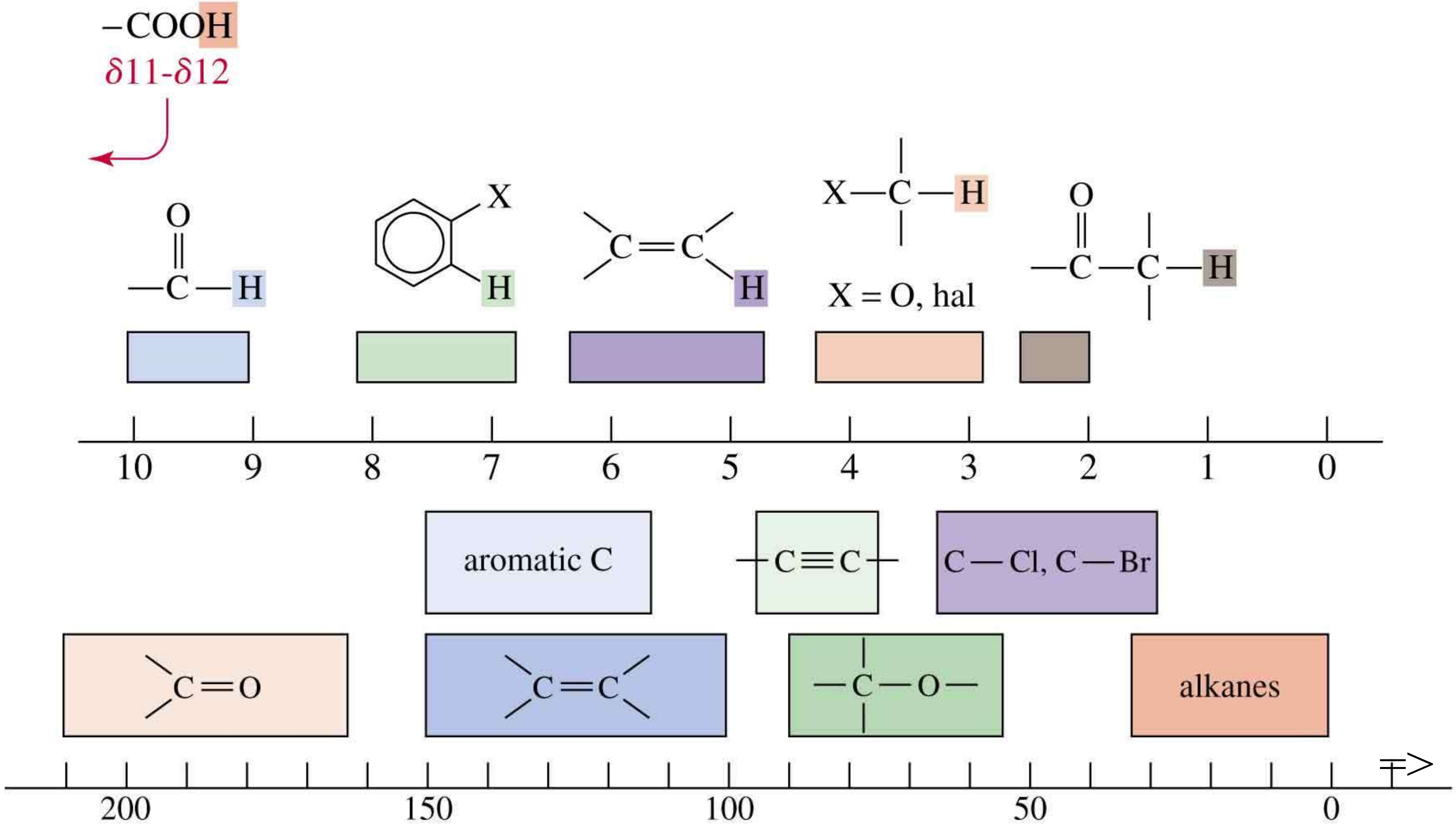


- Nuclei in a magnetic field are given a radio-frequency pulse close to their resonance frequency.
- The nuclei absorb energy and precess (spin) like little tops.
- A complex signal is produced, then decays as the nuclei lose energy.
- Free induction decay is converted to spectrum.

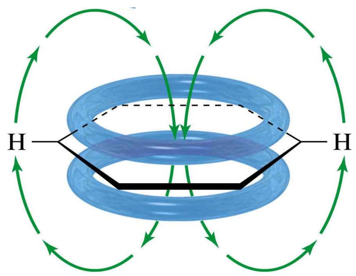
=>

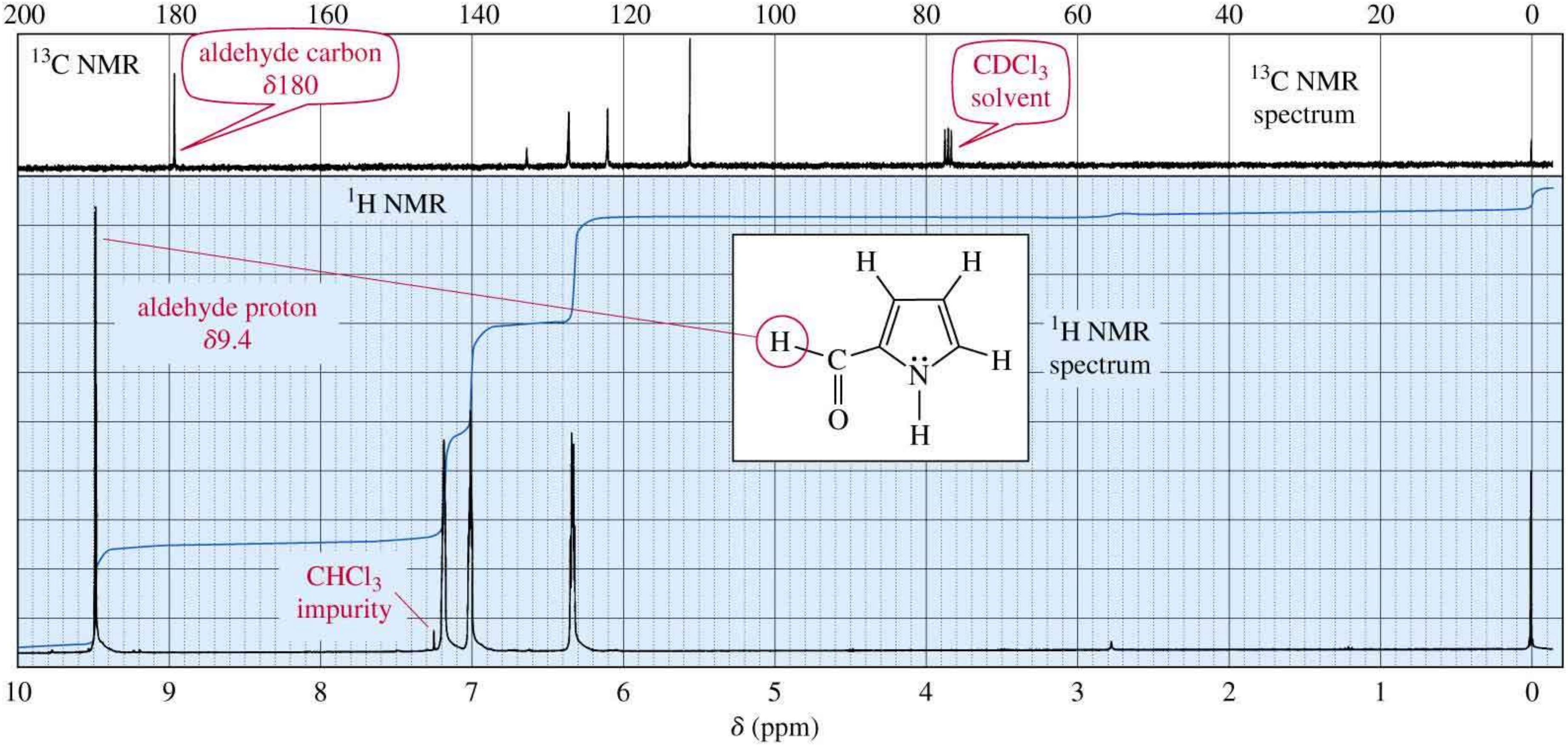
Hydrogen and Carbon Chemical Shifts





Combined ^{13}C and ^{1}H Spectra





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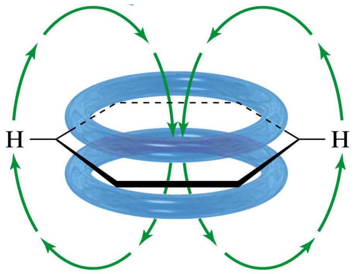
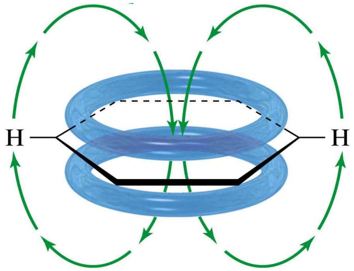
Differences in ^{13}C Technique



- Resonance frequency is ~ one-fourth, 15.1 MHz instead of 60 MHz.
- Peak areas are not proportional to number of carbons.
- Carbon atoms with more hydrogens absorb more strongly.

=>

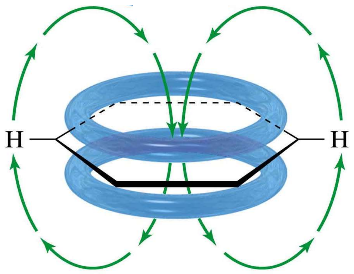


Spin-Spin Splitting

- It is unlikely that a ^{13}C would be adjacent to another ^{13}C, so splitting by carbon is negligible.
- ^{13}C will magnetically couple with attached protons and adjacent protons.
- These complex splitting patterns are difficult to interpret.

=>

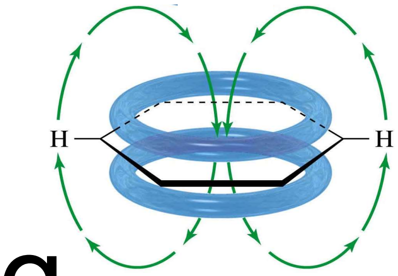
Proton Spin Decoupling



- To simplify the spectrum, protons are continuously irradiated with “noise,” so they are rapidly flipping.
- The carbon nuclei see an average of all the possible proton spin states.
- Thus, each different kind of carbon gives a single, unsplit peak.

=>

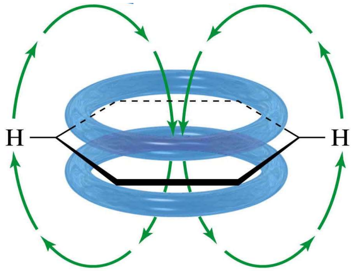
Off-Resonance Decoupling



- ^{13}C nuclei are split only by the protons attached directly to them.
- The *N* + 1 rule applies: a carbon with *N* number of protons gives a signal with *N* + 1 peaks.

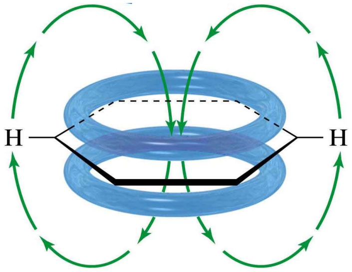
=>

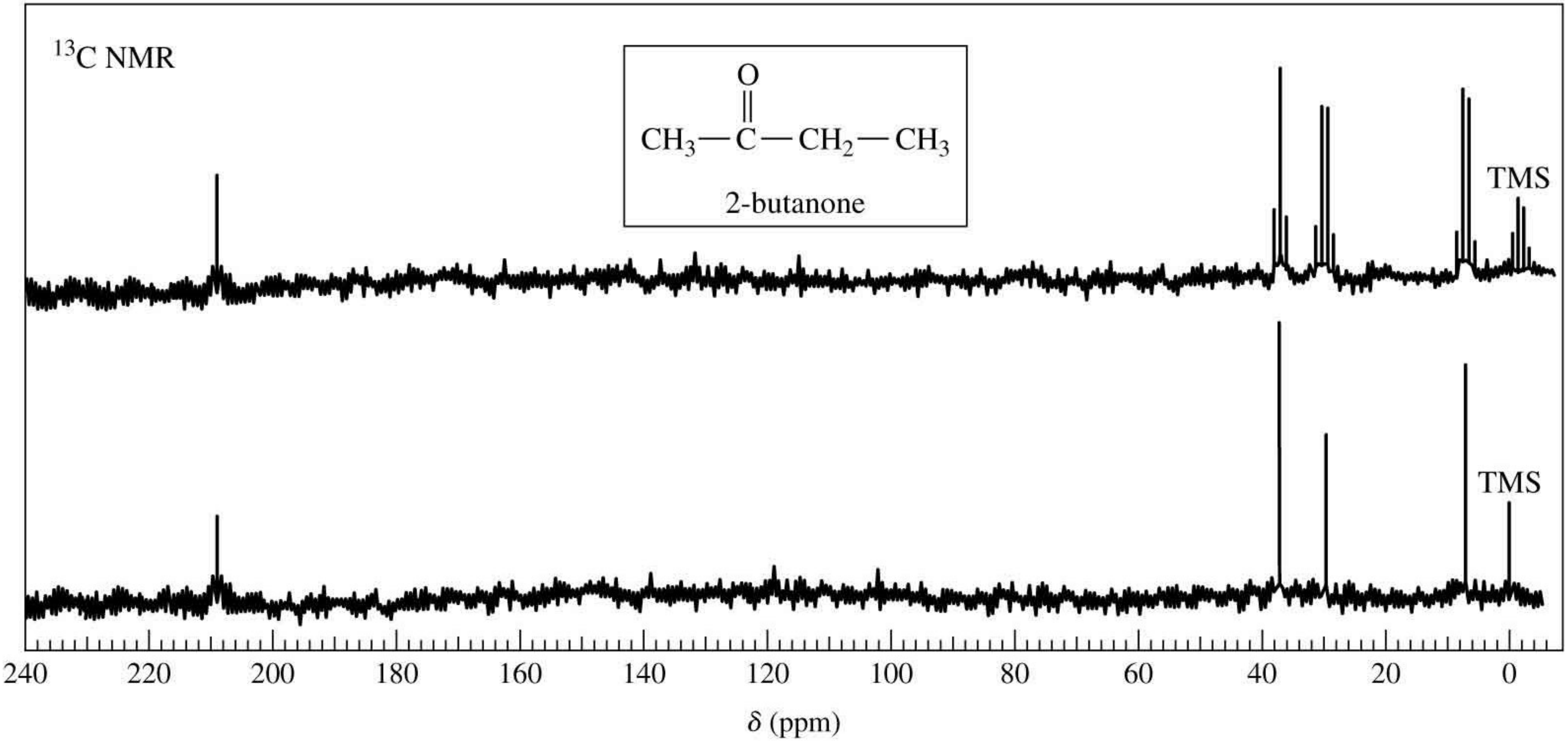
Interpreting ^{13}C NMR



- The number of different signals indicates the number of different kinds of carbon.
- The location (chemical shift) indicates the type of functional group.
- The peak area indicates the numbers of carbons (if integrated).
- The splitting pattern of off-resonance decoupled spectrum indicates the number of protons attached to the carbon. =>

Two ^{13}C NMR Spectra





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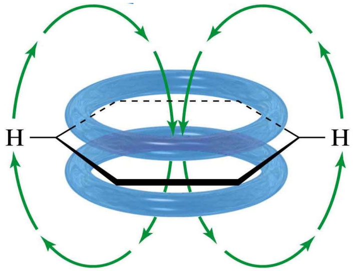
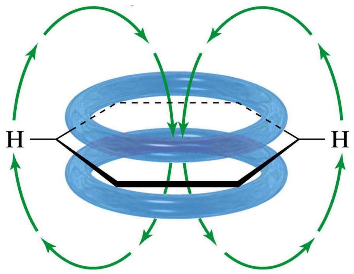
MRI



- Magnetic resonance imaging, noninvasive
- “Nuclear” is omitted because of public’s fear that it would be radioactive.
- Only protons in one plane can be in resonance at one time.
- Computer puts together “slices” to get 3D.
- Tumors readily detected.

=>



End of NMR

Photoelectron Spectroscopy

Photoelectron spectroscopy utilizes photo-ionization and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample.

Traditionally, when the technique has been used for surface studies it has been subdivided according to the source of exciting radiation in to :

X-ray Photoelectron Spectroscopy (XPS) - using soft x-rays (with a photon energy of 200-2000 eV) to examine core-levels.

Ultraviolet Photoelectron Spectroscopy (UPS) - using vacuum UV radiation (with a photon energy of 10-45 eV) to examine valence levels.

The development of synchrotron radiation sources has enabled high resolution studies to be carried out with radiation spanning a much wider and more complete energy range (5 - 5000+ eV) but such work remains a small minority of all photoelectron studies due to the expense, complexity and limited availability of such sources.

Physical Principles

Photoelectron spectroscopy is based upon a single photon in/electron out process and from many viewpoints this underlying process is a much simpler phenomenon than the Auger process.

The energy of a photon of all types of electromagnetic radiation is given by the Einstein relation :

$$E = h\nu$$

where

h - Planck constant (6.62×10^{-34} J s)
ν - frequency (Hz) of the radiation

Photoelectron spectroscopy uses monochromatic sources of radiation (i.e. photons of fixed energy).

In XPS the photon is absorbed by an atom in a molecule or solid, leading to ionization and the emission of a core (inner shell) electron. By contrast, in UPS the photon interacts with valence levels of the molecule or solid, leading to ionisation by removal of one of these valence electrons.

The kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyser and a photoelectron spectrum can thus be recorded.

The process of photoionization can be considered in several ways : one way is to look at the overall process as follows :

$$A + h\nu \rightarrow A^{+} + e^{-}$$

Conservation of energy then requires that :

$$E(A) + h\nu = E(A^{+}) + E(e^{-})$$

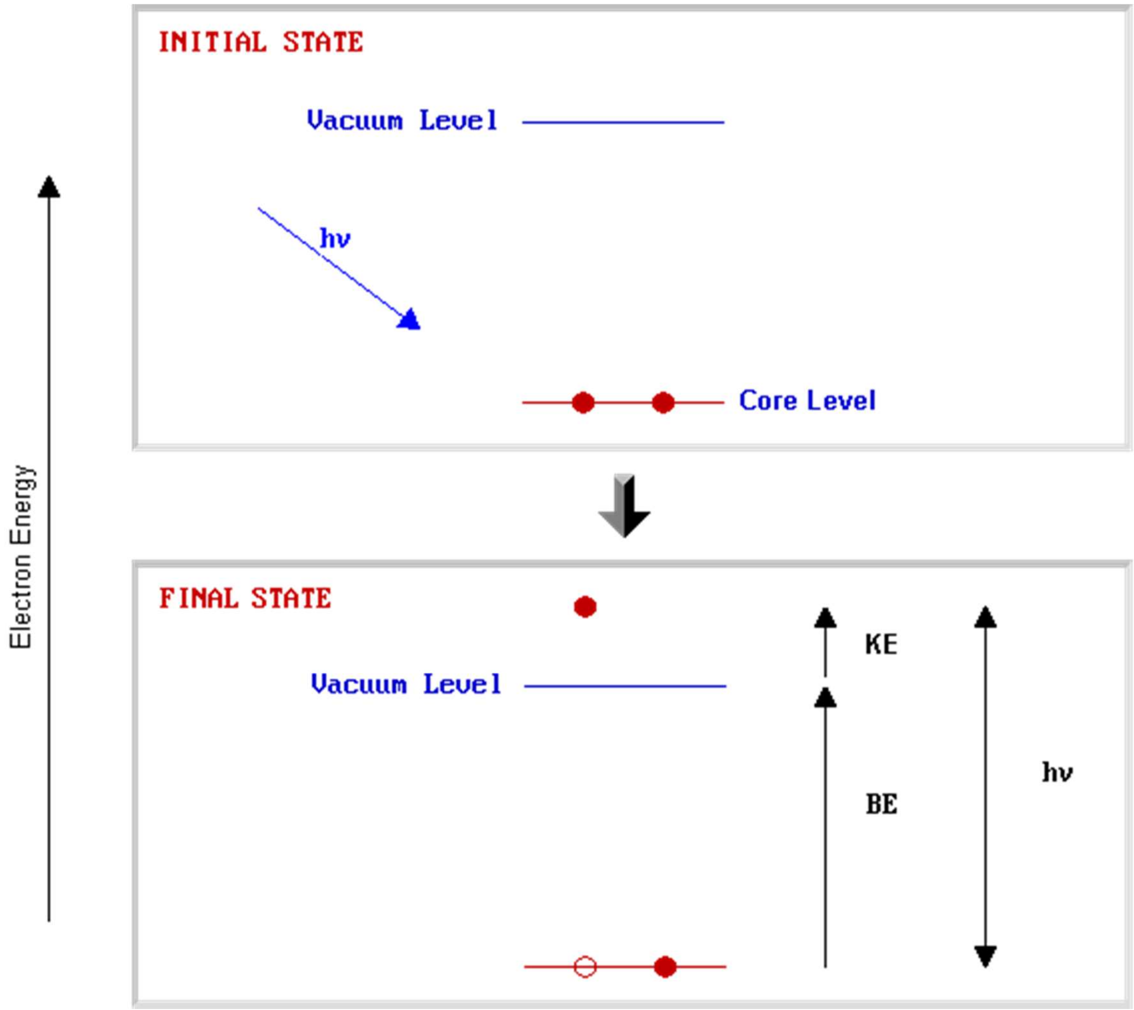
Since the electron's energy is present solely as kinetic energy (KE) this can be rearranged to give the following expression for the KE of the photoelectron:

$$KE = h\nu - (E(A^{+}) - E(A))$$

The final term in brackets, representing the difference in energy between the ionized and neutral atoms, is generally called the *binding energy* (BE) of the electron - this then leads to the following commonly quoted equation :

$$KE = h\nu - BE$$

An alternative approach is to consider a one-electron model along the lines of the following pictorial representation ; this model of the process has the benefit of simplicity but it can be rather misleading.



The BE is now taken to be a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level and the KE of the photoelectron is again given by :

$$KE = h\nu - BE$$

NOTE - the binding energies (BE) of energy levels in solids are conventionally measured with respect to the Fermi-level of the solid, rather than the vacuum level. This involves a small correction to the equation given above in order to account for the *work function* (ϕ) of the solid, but for the purposes of the discussion below this correction will be neglected.

Experimental Details

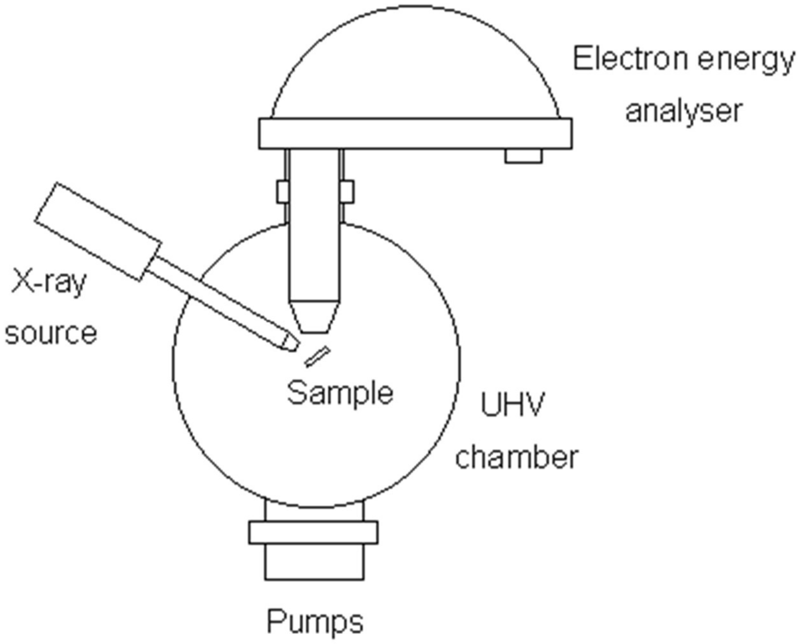
The basic requirements for a photoemission experiment (XPS or UPS) are:

1. a source of fixed-energy radiation (an x-ray source for XPS or, typically, a He discharge lamp for UPS)

2. an electron energy analyser (which can disperse the emitted electrons according to their kinetic energy, and thereby measure the flux of emitted electrons of a particular energy)

3. a high vacuum environment (to enable the emitted photoelectrons to be analysed without interference from gas phase collisions)

Such a system is illustrated schematically below:



There are many different designs of electron energy analyser but the preferred option for photoemission experiments is a concentric hemispherical analyser (CHA) which uses an electric field between two hemispherical surfaces to disperse the electrons according to their kinetic energy.

X-ray Photoelectron Spectroscopy (XPS)

For each and every element, there will be a characteristic binding energy associated with each core atomic orbital i.e. each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies.

The presence of peaks at particular energies therefore indicates the presence of a specific element in the sample under study - furthermore, the intensity of the peaks is related to the concentration of the element within the sampled region. Thus, the technique provides a *quantitative analysis of the surface* *composition* and is sometimes known by the alternative acronym , ESCA (Electron Spectroscopy for Chemical Analysis).

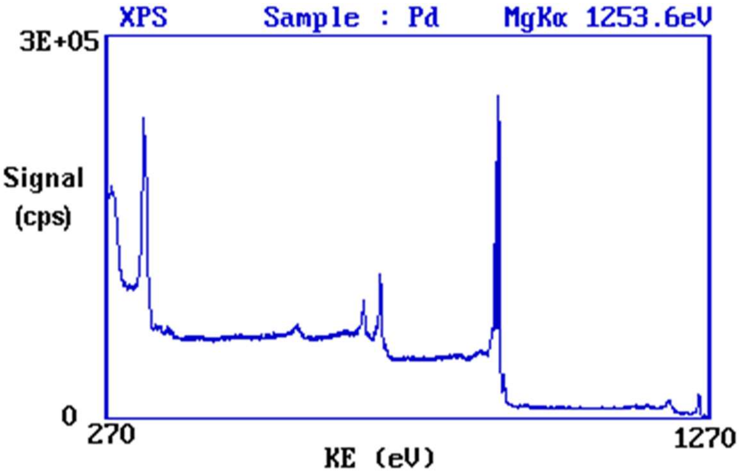
The most commonly employed x-ray sources are those giving rise to :

Mg K_α radiation : $h\nu$ = 1253.6 eV Al K_α radiation : $h\nu$ = 1486.6 eV

The emitted photoelectrons will therefore have kinetic energies in the range of *ca.* 0 - 1250 eV or 0 - 1480 eV . Since such electrons have very short IMFPs in solids (see Section 5.1) , the technique is necessarily surface sensitive.

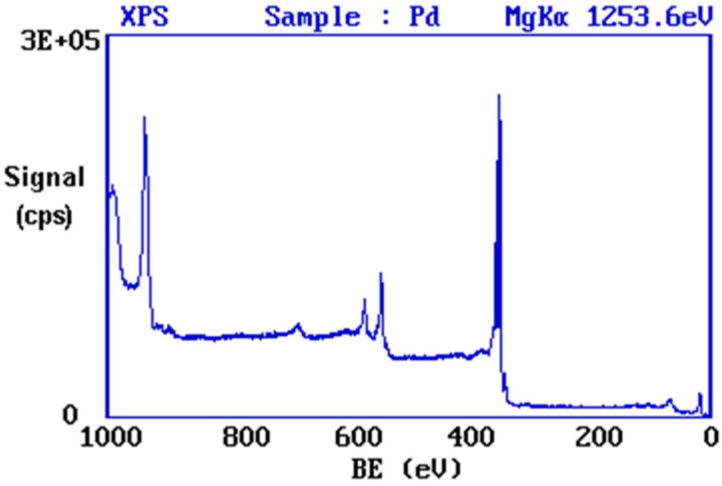
Example 1 - the XPS spectrum of Pd metal

The diagram below shows a real XPS spectrum obtained from a Pd metal sample using Mg K_α radiation



- the main peaks occur at kinetic energies of ca. 330, 690, 720, 910 and 920 eV.

Since the photon energy of the radiation is always known it is a trivial matter to transform the spectrum so that it is plotted against BE as opposed to KE.

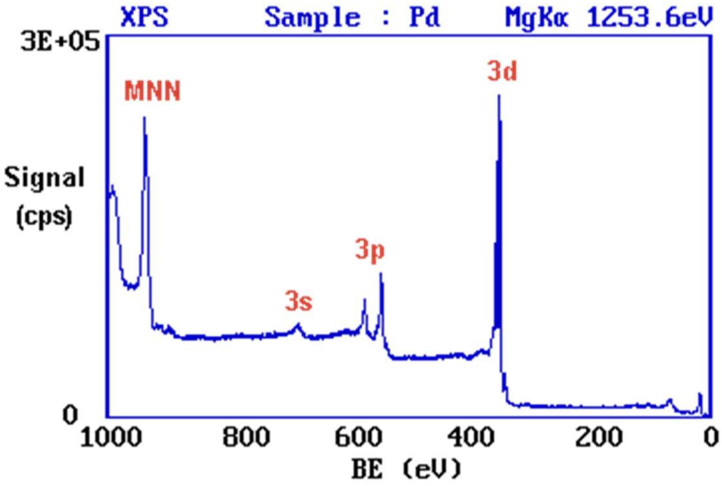


The most intense peak is now seen to occur at a binding energy of ca. 335 eV

Working downwards from the highest energy levels ......

1. the valence band (4*d*, 5*s*) emission occurs at a binding energy of *ca.* 0 - 8 eV (measured with respect to the Fermi level, or alternatively at ca. 4 - 12 eV if measured with respect to the vacuum level).
2. the emission from the 4*p* and 4*s* levels gives rise to very weak peaks at 54 eV and 88 eV respectively
3. the most intense peak at ca. 335 eV is due to emission from the 3*d* levels of the Pd atoms, whilst the 3*p* and 3*s* levels give rise to the peaks at ca. 534/561 eV and 673 eV respectively.
4. the remaining peak is not an XPS peak at all ! - it is an Auger peak arising from x-ray induced Auger emission. It occurs at a kinetic energy of ca. 330 eV (in this case it is really meaningless to refer to an associated binding energy).

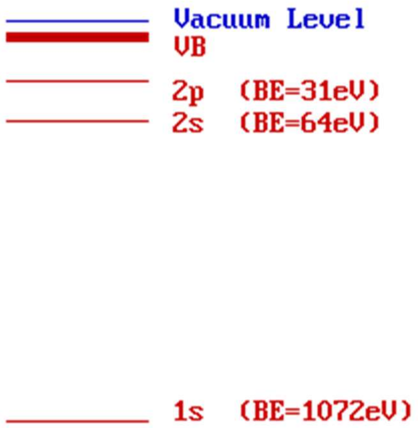
These assignments are summarised below ...



It may be further noted that

- there are significant differences in the natural widths of the various photoemission peaks
- the peak intensities are not simply related to the electron occupancy of the orbitals

Exercise 1 - the XPS spectrum of NaCl



The diagram opposite shows an energy level diagram for sodium with approximate binding energies for the core levels.

If we are using Mg K_α ($h\nu$ = 1253.6 eV) radiation ...

... at what kinetic energy will the Na 1s photoelectron peak be observed ?

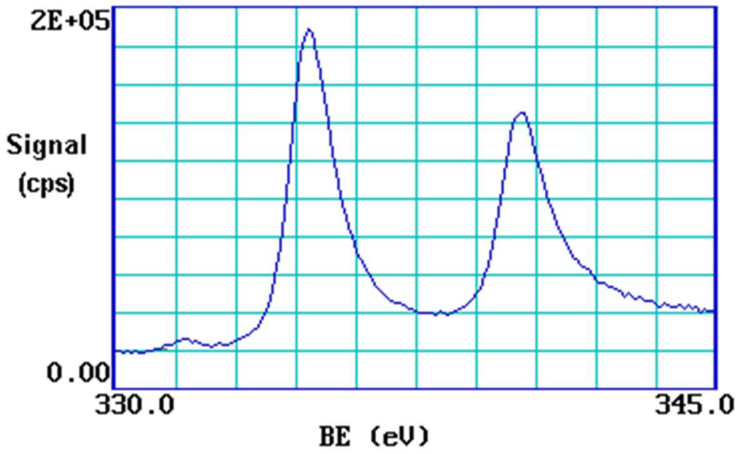
(the 1*s* peak is that resulting from photoionisation of the 1*s* level)

... at what kinetic energy will the Na 2s and 2p photoelectron peaks be observed ?

Spin-Orbit Splitting

Closer inspection of the spectrum shows that emission from some levels (most obviously 3*p* and 3*d*) does not give rise to a single photoemission peak, but a closely spaced doublet.

We can see this more clearly if, for example, we expand the spectrum in the region of the 3*d* emission ...



The 3*d* photoemission is in fact split between two peaks, one at 334.9 eV BE and the other at 340.2 eV BE, with an intensity ratio of 3:2 . This arises from spin-orbit coupling effects in the final state. The inner core electronic configuration of the initial state of the Pd is :

$(1s)^2\ (2s)^2\ (2p)^6\ (3s)^2\ (3p)^6\ (3d)^{10}$ ....

with all sub-shells completely full.

The removal of an electron from the 3*d* sub-shell by photo-ionization leads to a $(3d)^9$ configuration for the final state - since the *d*-orbitals (l = 2) have non-zero orbital angular momentum, there will be coupling between the unpaired spin and orbital angular momenta.

Spin-orbit coupling is generally treated using one of two models which correspond to the two limiting ways in which the coupling can occur - these being the *LS* (or Russell-Saunders) coupling approximation and the *j-j* coupling approximation.

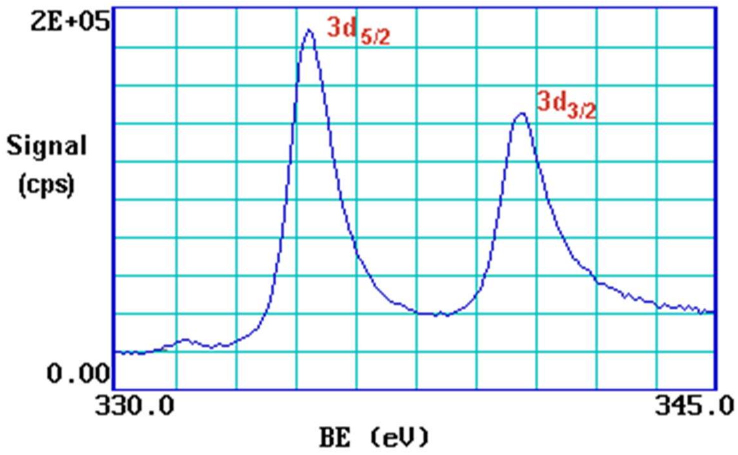
If we consider the final ionised state of Pd within the Russell-Saunders coupling approximation, the $(3d)^9$ configuration gives rise to two states (ignoring any coupling with valence levels) which differ slightly in energy and in their degeneracy ...

$^{2D}{}_{5/2}$ g_J = 2x{5/2}+1 = 6
$^{2D}{}_{3/2}$ g_J = 2x{3/2}+1 = 4

These two states arise from the coupling of the L = 2 and S = 1/2 vectors to give permitted J values of 3/2 and 5/2. The lowest energy final state is the one with maximum J (since the shell is more than half-full), i.e. J = 5/2, hence this gives rise to the "lower binding energy" peak. The relative intensities of the two peaks reflects the degeneracies of the final states ($g_J = 2J + 1$), which in turn determines the probability of transition to such a state during photoionization.

The Russell-Saunders coupling approximation is best applied only to light atoms and this splitting can alternatively be described using individual electron *l*-*s* coupling. In this case the resultant angular momenta arise from the single hole in the *d*-shell; a *d*-shell electron (or hole) has l = 2 and s = 1/2, which again gives permitted *j*-values of 3/2 and 5/2 with the latter being lower in energy.

The peaks themselves are conventionally annotated as indicated - note the use of lower case lettering



This spin-orbit splitting is of course not evident with *s*-levels (*l* = 0), but is seen with *p*,*d* & *f* core-levels which all show characteristic spin-orbit doublets.

Chemical Shifts

The exact binding energy of an electron depends not only upon the level from which photoemission is occurring, but also upon :

1. the formal oxidation state of the atom
2. the local chemical and physical environment

Changes in either (1) or (2) give rise to small shifts in the peak positions in the spectrum - so-called *chemical shifts* .

Such shifts are readily observable and interpretable in XP spectra (unlike in Auger spectra) because the technique :

- is of high intrinsic resolution (as core levels are discrete and generally of a well-defined energy)
- is a one electron process (thus simplifying the interpretation)

Atoms of a higher positive oxidation state exhibit a higher binding energy due to the extra coulombic interaction between the photo-emitted electron and the ion core. *This ability to discriminate between different oxidation states and chemical environments is one of the major strengths of the XPS technique.*

In practice, the ability to resolve between atoms exhibiting slightly different chemical shifts is limited by the peak widths which are governed by a combination of factors ; especially

- the intrinsic width of the initial level and the lifetime of the final state

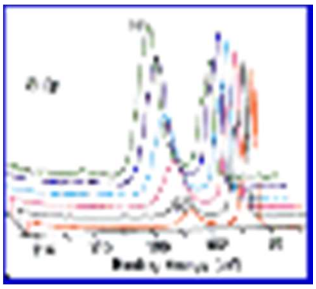
- the line-width of the incident radiation - which for traditional x-ray sources can only be improved by using x-ray monochromators
- the resolving power of the electron-energy analyser

In most cases, the second factor is the major contribution to the overall line width.

Angle Dependent Studies

As described in Section 5.1, the degree of surface sensitivity of an electron-based technique such as XPS may be varied by collecting photoelectrons emitted at different emission angles to the surface plane. This approach may be used to perform non-destructive analysis of the variation of surface composition with depth (with chemical state specificity).

Examples



Angle-dependent analysis of a silicon wafer with a native oxide layer
(courtesy of Physical Electronics, Inc. (PHI))

Ultraviolet Photoelectron Spectroscopy (UPS)

In UPS the source of radiation is normally a noble gas discharge lamp ; frequently a He-discharge lamp emitting He I radiation of energy 21.2 eV .

Such radiation is only capable of ionising electrons from the outermost levels of atoms - the valence levels. The advantage of using such UV radiation over x-rays is the very narrow line width of the radiation and the high flux of photons available from simple discharge sources. The main emphasis of work using UPS has been in studying :

1. the electronic structure of solids - detailed angle resolved studies permit the complete band structure to be mapped out in *k*-space.
2. the adsorption of relatively simple molecules on metals - by comparison of the molecular orbitals of the adsorbed species with those of both the isolated molecule and with calculations.